

US JAPAN WORKSHOP

HYBRID 2000 CONFERENCE

MAY 7-MAY 12, 2000

RAMADA INN

ITHACA, NEW YORK

REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington, DC 20503.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 05/31/01		2. REPORT DATE Technical		3. DATES COVERED (From - To) 15 - MAR - 2000 to 28 -Feb - 2001	
4. TITLE AND SUBTITLE U.S. - Japan Joint Workshop				5a. CONTRACT NUMBER N/A	
				5b. GRANT NUMBER N00014-00-1-0478	
				5c. PROGRAM ELEMENT NUMBER N/A	
6. AUTHOR(S) Giannelis, Emmanuel, P, Dr.				5d. PROJECT NUMBER 01PR12067-00	
				5e. TASK NUMBER N/A	
				5f. WORK UNIT NUMBER N/A	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Cornell University Materials Science & Engineering Ithaca, NY 14853-1501				8. PERFORMING ORGANIZATION REPORT NUMBER N/A	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) OFFICE OF NAVAL RESEARCH REGIONAL OFFICE BOSTON 495 SUMMER STREET ROOM 627 BOSTON MA 02210-2109				10. SPONSOR/MONITOR'S ACRONYM(S) ONR 244	
				11. SPONSORING/MONITORING AGENCY REPORT NUMBER N/A	
12. DISTRIBUTION AVAILABILITY STATEMENT No limitation					
13. SUPPLEMENTARY NOTES N/A					
14. ABSTRACT See attached "Workshop Brochure" <div style="text-align: center; font-size: 2em; font-weight: bold;">20011123 020</div>					
15. SUBJECT TERMS Symposium					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 49	19a. NAME OF RESPONSIBLE PERSON E.P. Giannelis
a. REPORT N/A	b. ABSTRACT N/A	c. THIS PAGE N/A			19b. TELEPHONE NUMBER (Include area code) (607) 255-9680

US JAPAN WORKSHOP
HYBRID 2000 WORKSHOP

MAY 8 - MAY 12, 2000

Orgnaizers: Emmanuel P. Giannelis (Cornell University)
Kazuyuki Kuroda (Waseda University)

Sponsors: CCMR-Cornell Center for Materials Research
Office of Naval Research
Department of Materials Science

US JAPAN WORKSHOP
HYBRID 2000 WORKSHOP

MAY 7 - MAY 12, 2000
Program

Sunday May 7th Arrival at Ramada Inn 2-5PM

Monday May 8th 8AM Registration-name tags

Session Chair: K. Wynne

8:45 Welcome

9-9:45 " Hybrid Phosphazene-Organic, Phosphazene-Organosilicon, and Other New Materials by Living Cationic Polymerization", Harry Allcock (The Pennsylvania State University)

9:45-10:30 "Polymerization of $X_3P=N-P(O)X_2$ Under the Various Conditions", Meisetsu Kajiwara (Gifu University)

10:30-10:45 BREAK

10:45-11:30 "Chemistry of the Cubeoctameric Silicate Anion and Its application to the Synthesis of Organic-Inorganic Hybrids", Isao Hasegawa (Gifu University)

11:30-12:15 "Organic/inorganic Nanocomposites From Cubic Silsesquioxanes", Richard Laine (University of Michigan)

12:30-2:00 LUNCH-family style

Session Chair: Y. Chujo

2-2:45 "Polycarbosilanes: Precursors to Ceramics and Novel Inorganic-organic Hybrid Polymers", Leonard Interrante (Rensselaer Polytechnic Institute)

2:45-3:30 "Silicon Carbide Ceramics Formation from Cross-Linked Polysilane Co-Polymer Precursors", Masaki Narisawa (Osaka Prefecture University)

3:30-3:45 BREAK

3:45-4:30 "Sila-functional Oligosiloxanes, Silsesquioxanes, and Hybrids", Yoshimoto Abe (University of Tokyo)

4:30-5:15 "Well-Defined Organic/Inorganic Hybrids By Atom Transfer Radical Polymerization", Krzysztof Matyjaszewski (Carnegie Mellon University)

6PM DINNER @ HEIGHTS CAFÉ

Tuesday May 9th 8AM Registration-name tags

Session Chair: K. Kuroda

9-9:45 "New π -Conjugated Boron -Containing Polymers", Yoshiaki Chujo (Kyoto University)

9:45-10:30 "Dynamic and Selective Responses of Organically-Modified Silica Sol-Gels", Bakul C. Dave (Southern Illinois University)

10:30-10:45 BREAK

10:45-11:30 "Nano-Objects With Controlled Shape, Size and Composition From Block Copolymer-Ceramic Hybrid Materials", Ulrich Wiesner (Cornell University)

11:30-12:15 "Solid-state NMR Investigation on Organically-Modified Ceramics Prepared from Alkoxysilanes", Yoshiyuki Sugahara (Waseda University)

12:30 depart for Corning Glass Museum Tour Box lunches provided by Ramada Inn

5:30PM drop off at MV Manhattan for dinner cruise 6PM-9PM bus to pick up and return to hotel at 9:15PM --**will need orders ahead of time will try to get people to look over menu on Monday at a break or lunch time

Wednesday May 10th 8AM Registration

Session Chair: K. Matyjaszewski

9-9:45 "Elastomers From Dihydroxy-Polydimethylsiloxane and Alkoxysilanes: Surface Microstructures and Surface Characterization", Kenneth Wynne (Office of Naval Research)

9:45-10:30 "Zirconium-Containing Organic-Inorganic Polymer Hybrids", Takahiro Gunji (Science University of Tokyo)

10:30-10:45 BREAK

10:45-11:30 Keiichi Moriya (Gifu University)

11:30-12:15 Nora Beck-Tan (Army Research Lab) Cancelled

12:30-2PM Deli Lunch

2PM depart for Wine tour @ Swedish Hill-(2:45-4:30) and Goosewatch (4:35 -5:05PM)wineries. Return to hotel by 6PM

Thursday May 11th 8AM Registration

Session Chair: R. Laine

9-9:45 "Mesoscopic Structure of Polymer-Inorganic

Nanocomposites: Impact on Chain Behavior and Physical

Properties", Richard Vaia, (Air Force Research Laboratory)

9:45-10:30 "An Efficient Encapsulation of colloidal Silica by
Emulsion Polymerization of Acrylates. A facile Simple Approach
to Obtain Hybrid Materials with Controlled Properties",

Yoshiharu Kimura (Kyoto Institute of Technology)

10:30-10:45 BREAK

10:45-11:30 "Preparation of Organically Modified Layered
Silicates", Kazuyuki Kuroda (Waseda University)

11:30-12:15 "Interphase Structure and Dynamics In Polymer
Nanocomposites", Emmanuel Giannelis (Cornell University)

12:30-2PM Deli Lunch

Thursday PM depart from Ithaca.

ABSTRACTS
OF
PRESENTATIONS

HYBRID PHOSPHAZENE-ORGANIC, PHOSPHAZENE-ORGANOSILICON, AND OTHER NEW MATERIALS BY LIVING CATIONIC POLYMERIZATION

Harry R. Allcock
Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania, 16802, U.S.A.

A recently developed method for the synthesis of polyphosphazenes by a living, cationic, ambient temperature polymerization of phosphoranimines has allowed access to a wide range of new hybrid structures. These include polymers with controlled molecular weights and narrow polydispersities, block copolymers with organic polymers and poly(dimethylsiloxane), and star polymers. In addition, two new methods for the linkage of cyclic phosphazenes to classical organic polymers will be described. The new polymers are of interest as biomedical materials, fire-resistant polymers, and materials for aerospace applications.

POLYMERIZATION OF $X_3P=N-P(O)X_2$ UNDER THE VARIOUS CONDITIONS

Meisetsu KAJIWARA

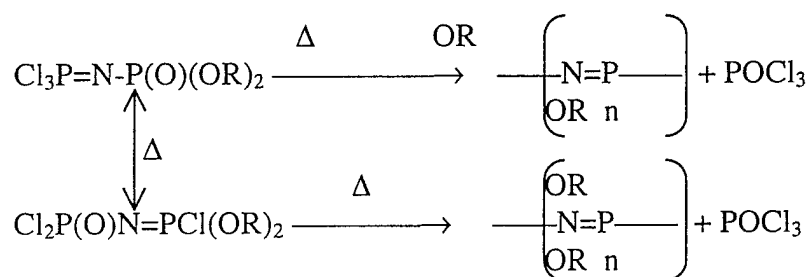
School of Dentistry, Aichi-Gakuin University, 1-100 Kusumoto-cho, Chikusa-ku, Nagoya 464-0034, Japan

Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-0814, Japan

As for the standard synthetic route for polyorganophosphazenes, (1) polydichlorophosphazene was prepared by ring-opening polymerization of hexachlorocyclotriphosphazene, and then (2) polyorganophosphazenes were formed with the reaction between polydichlorophosphazene and nucleophilic reagents such as alkoxides, phenoxides and amine compounds. The second way to prepare polyorganophosphazenes was condensation of $ROR_2P=NSiMe_3$. Recently, Prof. Allcock reported the "living" cationic polymerization of phosphoramines as an ambient temperature route to polyphosphazenes with controlled molecular weights. The new method involved the initiation of $Cl_3P=NSiMe_3$ with a small amount of PCl_5 in CH_2Cl_2 to yield polydichlorophosphazenes.

Prof. Jaeger and Atochem Co. described a new access route of polydichlorophosphazene which depended on the polymerization of N-(dichlorophosphoryl)-P-(trichloromonophosphazene) $Cl_3P=N-P(O)Cl_2$ (I). To prepare polydichlorophosphazene or polyorganophosphazene with the new route or methods, (I) was polymerized with γ -irradiation. The polymer was not prepared under the conditions, however, the polymer was formed by heating and flowing oxygen gas.

Also, new precursors such as $Cl_3P=N-P(O)(OR)_2$ (II) were prepared with the reaction of PCl_5 and $(RO)_2P(O)NH_2$. (II) was polymerized by heating or at ambient temperature with or without solvents and catalysts.



Chemistry of the Cubeoctameric Silicate Anion and Its Application to the Synthesis of Organic-Inorganic Hybrids

Isao Hasegawa

Department of Chemistry, Faculty of Engineering, Gifu University
Yanagido 1-1, Gifu-City, Gifu 501-1193, Japan

We have been studying on the synthesis of the cubeoctameric silicate ($\text{Si}_8\text{O}_{20}^{8-}$)-dimethylsiloxane hybrids [1]. The objective of the study is to control over the structure of their silica (SiO_2) component, that is, the nanostructure of the hybrids.

Hybrids in the SiO_2 -dimethylsiloxane system have also been prepared from tetraethoxysilane [$\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS] and silanol-terminated polydimethylsiloxanes by a sol-gel reaction [2], which are one of the most well-known Ormosils (for organically modified silicates). Since it is usually difficult to control hydrolysis and polycondensation reactions of TEOS, the structure of SiO_2 clusters involved in the hybrids would not be well-controlled. If the size of the clusters is too large, the hybrids would be brittle as SiO_2 gels and glasses are. Thus, the control over the structure of SiO_2 component is an important issue for this type of hybrids. For this purpose, the $\text{Si}_8\text{O}_{20}^{8-}$ silicate species has been used as the starting material in our studies and reactions have been carried out so that the hybrids has the higher-order structure that the silicate structure is present as the building block.

The $\text{Si}_8\text{O}_{20}^{8-}$ silicate anion can be produced at a high yield as both soluble species in methanol [3] and a solid [4]. Hydrolysis of tetraalkoxysilane in a methanol solution of tetramethylammonium hydroxide containing water leads to the selective formation of the species. Vigorous stirring of a mixture of TEOS and an aqueous solution of (2-hydroxyethyl)trimethylammonium (choline) hydroxide results in the formation of solid choline silicate which is comprised of the $\text{Si}_8\text{O}_{20}^{8-}$ structure. Concerning reaction of the $\text{Si}_8\text{O}_{20}^{8-}$ silicate anion, there are two useful reactions: (1) reaction with monochlorosilane in 2,2-dimethoxypropane [5] and (2) condensation reaction in methanol [6]. Reaction (1) can be used for production of a variety of organic derivatives of $\text{Si}_8\text{O}_{20}^{8-}$. Reaction (2) takes place without breakdown of the $\text{Si}_8\text{O}_{20}^{8-}$ structure. Synthesis procedures for the $\text{Si}_8\text{O}_{20}^{8-}$ -dimethylsiloxane hybrids are based on these reactions.

In this talk, synthesis conditions and reactions of $\text{Si}_8\text{O}_{20}^{8-}$ and two procedures for producing the $\text{Si}_8\text{O}_{20}^{8-}$ -dimethylsiloxane hybrids are presented.

References

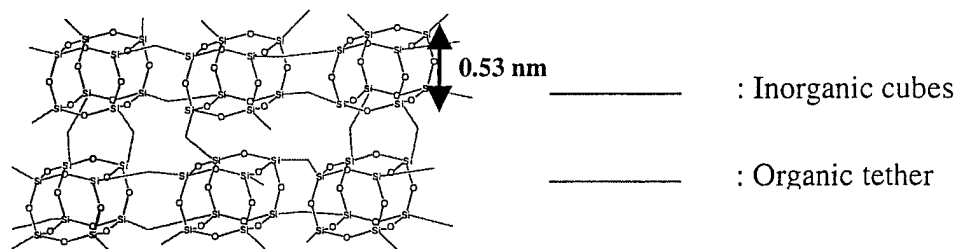
- [1] I. Hasegawa, *Recent Res. Devel. in Pure & Applied Chem.*, **2**, 573 (1998). [2] J.D. Mackenzie, *Mater. Technol.*, **11**, 1 (1996). [3] (a) I. Hasegawa *et al.*, *J. Mol. Liq.*, **34**, 307 (1987). (b) I. Hasegawa *et al.*, *J. Chem. Soc., Chem. Commun.*, **1989**, 208. [4] I. Hasegawa and S. Sakka, *Chem. Lett.*, **1988**, 1319. [5] (a) I. Hasegawa and S. Motojima, *J. Organomet. Chem.*, **441**, 373 (1992). (b) I. Hasegawa *et al.*, *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 1099 (1994). [6] I. Hasegawa, *Zeolites*, **12**, 720 (1992).

Organic/inorganic nanocomposites from cubic silsesquioxanes.

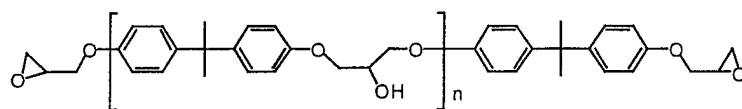
Ji-Won Choi and Rickard. M. Laine

Departments of Materials Science and Eng., Chemistry and the Macromolecular Science and Eng. Center, University of Michigan, Ann Arbor, MI.

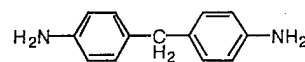
Introduction: Our goal is to develop structure-property-processing relationships in nanocomposites prepared using octa-functionalized silsesquioxanes $[(\text{RSiO})_{1.5}]_8$, cubes) to establish a complete understanding of the behavior of "interphase" materials. Interphase materials normally consist of the species at the interfaces between adjacent phases. In our approach, organic functional groups ($\text{R} = \text{epoxy, methacryloyl, etc}$) are appended to inorganic cubes and polymerized to give organic/inorganic nanocomposites wherein both components are present at the 1~2 nm scale and discontinuous. Their properties will be governed not only by the nature of but also by the scale of each phase. Thus, all organic and inorganic species are at discontinuous interfaces at length scales typical of interphase materials and the composites should be wholly interphase.



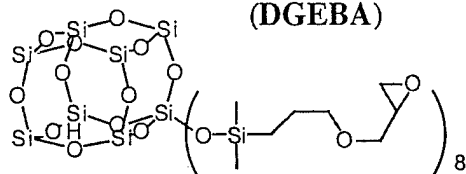
Scope of the current work: To achieve our goal, we are exploring the effects of varying the architecture of the organic phase between cubic silsesquioxanes in these nanocomposites on their physical properties. We also expect to develop strong/tough and thermally stable nanocomposites. Two kinds of epoxy-functionalized cubes with similar molecular weights were synthesized and cured using DDM shown below. Their thermal and mechanical properties were tested and compared with those of the commercial epoxy resin (DGEBA/DDM). As shown below, subtle changes in the rigidity, structure and the length of the organic tether result in noticeable differences in macroscopic properties.



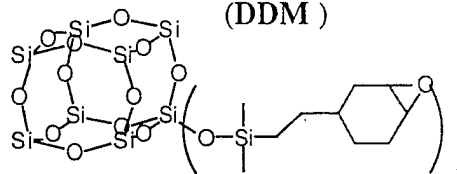
Diglycidyl ether of bisphenol A
(DGEBA)



Diaminodiphenylmethane
(DDM)

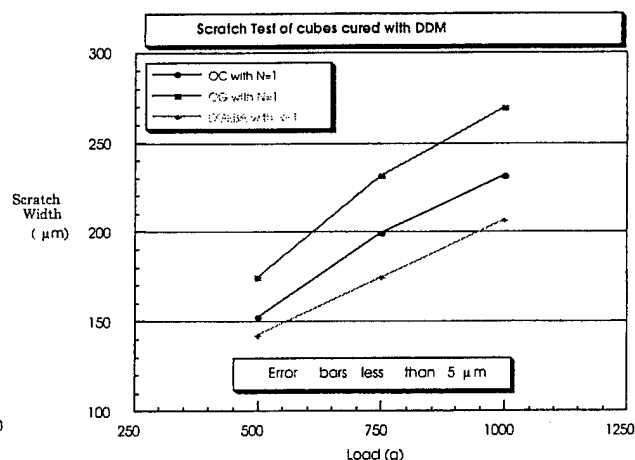
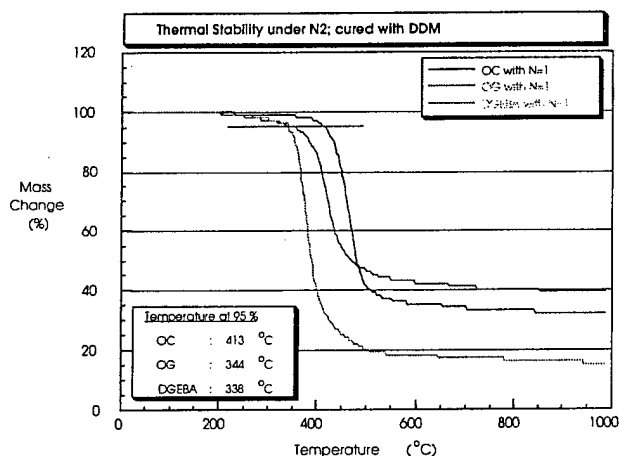
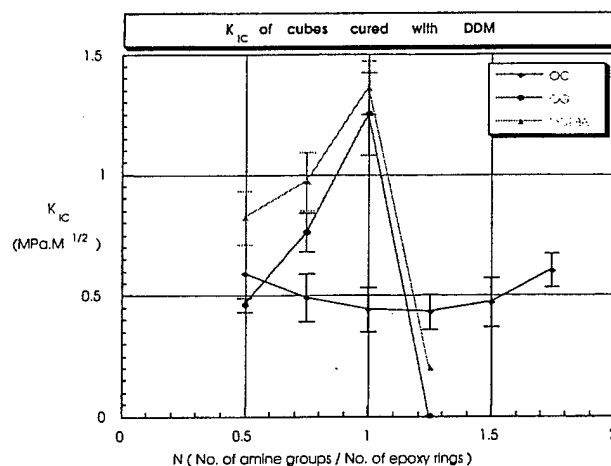
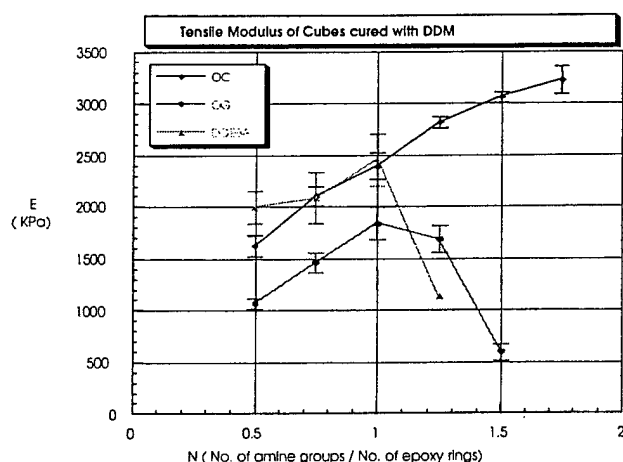


Octa(dimethylsiloxypropylglycidylether) cube
(OG)



Octa(dimethylsiloxycyclohexenyl-epoxide) cube
(OC)

Data:



Importance: Cube composites show excellent thermal stability (compared to DGEBA/DDM) and good mechanical properties. Furthermore, the addition of one more carbon and cyclization of the organic tether in OC (vs OG nanocomposites) caused significantly different mechanical behavior, indicating a “nonlinear relationship” between the macroscopic properties and the organic architecture for identical length scales. Further manipulation of the organic phases should eventually lead to further improvements in thermal stability and strong/tough materials, as we develop a detailed understanding of structure-property-processing relationships of these “interphase” nanocomposites. Future work includes modifying the epoxy chains, developing amine-functionalized cubes to replace DDM and incorporating other polymerizable groups on the cubes to expand the types of organic tether under study and to eventually establish general trend.

Reference:

1. C. Zhang, et al., *J. Am. Chem. Soc.*, 120, 8380 (1998).
2. S. L. Kim, et al., *Polym. Eng. Sci.*, 18, 1093 (1978).

POLYCARBOSILANES: PRECURSORS TO CERAMICS AND NOVEL INORGANIC-ORGANIC HYBRID POLYMERS

Leonard Interrante, Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590

Our current research centers on the synthesis, properties and pyrolysis chemistry of poly(carbosilanes), Si-C backbone polymers which combine a non-polar, chemically stable, backbone structure with the functionalization ability that is characteristic of appropriately substituted Si atoms [Si-X (Cl, H, OR)]. In addition to the fundamental interest in these systems as analogs of important organic polymers (see below), they are also of interest as both precursors to ceramics and as a source of functional polymeric materials, e.g., polymer electrolytes. Over the past 14 years, we have developed effective synthetic routes to both linear and hyperbranched methylene-bridged polycarbosilanes having the compositional formula, "[RR'SiCH₂]_n", and have examined several of these polymers as precursors to Si-based ceramics such as SiC and SiO_xC_y. In the course of this work, the monosilicon analogs of both polyethylene and polyvinylidene fluoride have been prepared and studied, and a route to a relatively low cost SiC precursor ("HPCS") has been developed which is now being scaled up for large scale commercial use as a source of SiC matrices for SiC_f/SiC_m composites.

Silicon Carbide Ceramics Formation from Cross-Linked Polysilane Co-Polymer Precursors"

Masaki Narisawa, Yasumasa Hibi, Takashi Iseki, Kiyohito Okamura, Takaaki Dohmaru*, Kunio Oka*

Division of Engineering, Graduate Schools, Osaka Prefecture University

*Research Institute for Advanced Science and Technology, Osaka Prefecture University

1. Introduction

Precursor methods are useful for the synthesis of non-oxide ceramic materials with unique forms and microstructures. Since the original work on PCS derived from polydimethylsilane (PDMS), many efforts have been made to design new SiC precursors. Most polysilanes are, however, considered to be inappropriate silicon carbide precursors, because of their facile chain scission during thermolysis. One exception is polymethylsilane (PMS). The C/Si ratio in the starting PMS is 1, and Si-H bonds in PMS should play an important role in improving the ceramic yield. We report the reflux treatment of PMS itself and poly(methylsilane-dimethylsilane) co-polymers (P(MS-DMS)) in terms of cross-linking and ceramization.

2. Experimental

PMS and P(MS-DMS) were synthesized with a typical Wurtz reaction. P(MS/DMS)-7, 5, 3 were prepared from the monomer mixtures, in which the molar ratios of methyl dichlorosilane for the starting silanes are controlled at 0.7, 0.5 and 0.3. 1.0 g of the synthesized co-polymer was put into a long pyrex tube cell equipped with a condenser. The cell was evacuated, and filled with Ar. The precursor was heated up to an appointed temperature (423-723K) with a heating rate of 10 K/min under an Ar gas flow. The holding time at a maximum temperature was 1h.

3. Results

The starting PMS and co-polymers are viscose white liquid. ^{29}Si -NMR spectra of the obtained precursors show signals at -34 ppm ($\text{Si}(\text{C}_2\text{Si}_2)$) and -63 ppm ($\text{Si}(\text{C}_1\text{H}_1\text{Si}_2)$). The relative intensity of these signals depends on the starting chemical composition of the precursors. As the reflux temperature increases up to 573K, the intensity of -34 ppm and -63 ppm signals decreases and the shoulder at -74 ppm ($\text{Si}(\text{C}_1\text{Si}_3)$) increases, which indicate the formation of Si-Si network. Beyond 573K, new signals at 0 ppm ($\text{Si}(\text{C}_4)$) and -18 ppm ($\text{Si}(\text{C}_3\text{H}_1)$) arise, which indicate the formation of Si-C network. Si-Si cross-linking is

remarkable in the precursor having a large amount of methylsilane units in its chain structures. Such Si-Si cross-linking is also effective to increase the ceramic yield after pyrolysis.

Sila-functional Oligosiloxanes, Silsesquioxanes, and Hybrids

Yoshimoto ABE and Takahiro Gunji

Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Phone +81+471+24+1501(ex 3608), Fax +81+471+23+9890

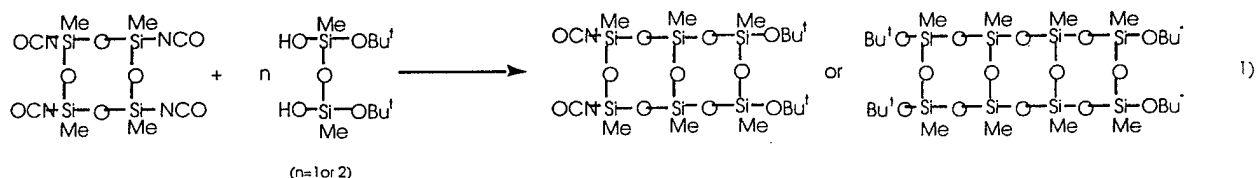
e-mail abeyoshi@ci.noda.sut.ac.jp

Polyphenylsilsesquioxane is well-known as a ladder type polysiloxane, but the structure is not still well-defined and controlled yet. Nevertheless polysilsesquioxanes have been noted as a potential candidate to provide the materials with excellent chemical, physical, and electrical properties. Therefore, the trend of recent research is in the structure control and synthesis of polysilsesquioxanes. Ladder polymethylsilsesquioxane as well as phenyl one is expected to be an another target material, and it has recently been prepared, though the structure is not well-controlled but sudo-ladder.

In the present paper, the results on the synthesis and properties of polymethylsilsesquioxane will be briefly summarized first and then the preparation of novel methylsilsesquioxanes with two or three eight-membered fused ring will be reported together with that of sila-functional oligosiloxanes as a starting material for silsesquioxanes.

Polymethylsilsesquioxane PMSQ with good spinnability and stability to self-condensation was synthesized by the method described and the results on the investigation of PMSQ as coatings showed that it strongly adheres to the organic and inorganic substrates to form sub-micrometer thin films with high transparency, thermal stability, and hardness depending on the polymer structure and curing times. It was also revealed to be a good precursor for interlayer low dielectric materials of electronic devices and moreover silicon oxycarbide ceramics.

Polymethylsilsesquioxane with ladder structure is an attractive compound from the view point of the structure and properties but it must be difficult to obtain. At present, therefore, the model compounds were synthesized by the reaction of silafunctional oligosiloxanes according to eq. 1) and identified to be the oligo methylsilsesquioxanes with two and three eight-membered fused rings.



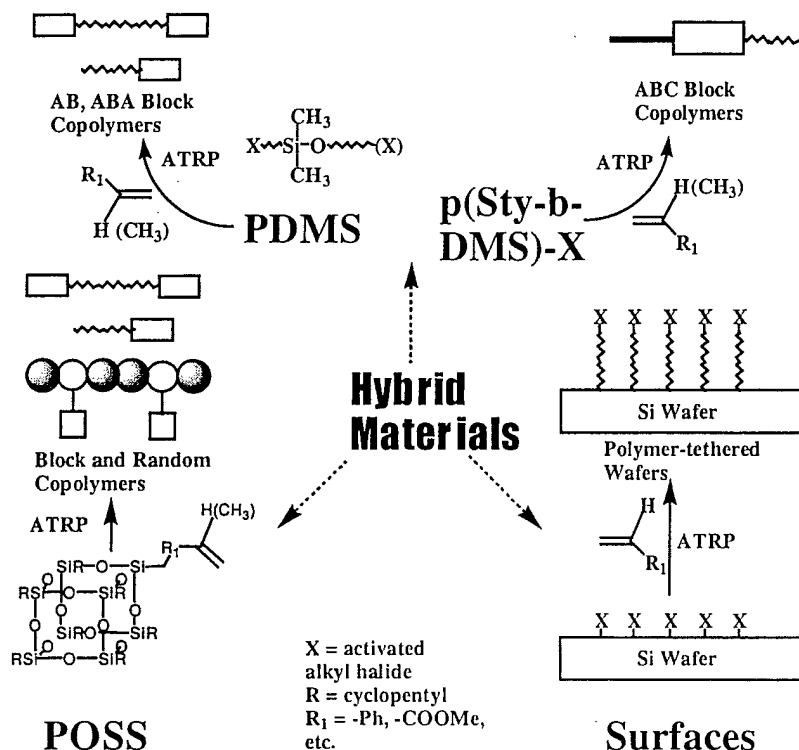
WELL- DEFINED ORGANIC/INORGANIC HYBRIDS BY ATOM TRANSFER RADICAL POLYMERIZATION

Krzysztof Matyjaszewski

*Center for Macromolecular Engineering, Department of Chemistry,
Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213*

Many synthetic methods have been reported for the preparation of organic/inorganic hybrid materials. Traditional approaches include the use of sol-gel chemistry to synthesize ceramic materials with polymeric components either covalently bound or interpenetrated with the inorganic phase. Alternatively, inorganic/organometallic monomers and polymer systems can be combined with their organic counterparts to prepare hybrid polymers with inorganic blocks, or pendant groups.

Through the utilization of inorganic (macro)initiators or monomers, atom transfer radical polymerization (ATRP) has been demonstrated to be a versatile method for the preparation of hybrid materials. ATRP has been successfully used to synthesize a variety of well-defined (co)polymers from acrylates, methacrylates and styrenes. Through this approach, poly(dimethylsiloxane) (PDMS) and silicon wafers, functionalized with initiator groups, have been used as macroinitiators for ATRP for the preparation of hybrid materials. Similarly, inorganic monomers have been (co)polymerized by ATRP from organic (macro)initiators. Specifically, polyhedral oligomeric silsesquioxane (POSS) monomers have been utilized for the synthesis of hybrid polymers. Different approaches towards well-defined organic/inorganic hybrids are summarized schematically below and will be discussed in detail.



2. ABSTRACT

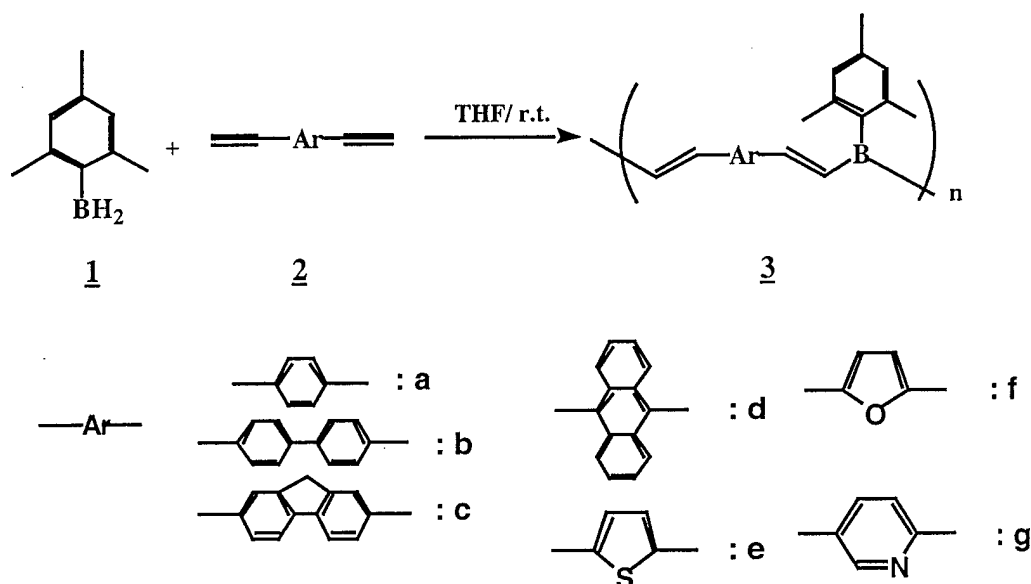
The objective of this three year research program is to **develop polymer nanocomposites as a new family of advanced materials for efficient solar energy harvesting.** This objective will be accomplished through collaborative efforts between four research groups at Cornell University (CU), the Oak Ridge National Laboratory (ORNL) and the University of Rochester (RU). The ORNL group, headed by Hu, will lead the synthesis of the nanoparticles and their coatings. At CU, the group headed by Giannelis will lead the development of the polymers and the dispersion of the nanoparticles in the polymers. At RU, the group headed by Rothberg will carry out optical measurements in order to understand the photophysical properties of the polymer nanocomposites that are relevant to solar cell performance. Finally, in the group headed by Malliaras at CU, the charge transport properties of the polymer nanocomposites will be studied by both steady-state and transient current measurements, coupled with photoinduced time-of-flight measurements. Model solar cells will be prepared and studied with a combination of (photo-)electrical characterization techniques, analytical theory and computer simulations in order to understand the relationship between device physics and optoelectronic properties of these materials. This program will lead to the fabrication of high efficiency solar cells at a low cost and will advance our fundamental knowledge of the optoelectronic properties of materials on the nanometer length scale.

NEW π -CONJUGATED BORON-CONTAINING POLYMERS

Yoshiki CHUJO

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

We have recently explored new methodologies for the preparation of organoboron mainchain polymers.¹ These include hydroboration, haloboration, phenylboration, allylboration and alkoxyboration polymerizations.² Especially, hydroboration polymerization between dienes and monoalkylboranes produced trialkylborane repeating polymers, which could be used as a novel type of reactive polymers.³ Thus, a wide variety of polymers having various functional groups were prepared starting from these organoboron mainchain polymers.⁴ On the other hand, hydroboration polymerization of diynes with monoalkylboranes gave organoboron polymers having dialkenylborane repeating units.⁵ Here we wish to describe hydroboration polymerization of aromatic diynes with mesitylborane, which gives novel π -conjugated organoboron mainchain polymers (Scheme 1).⁶



Scheme 1

The polymers obtained were highly soluble in common organic solvents such as THF, chloroform, and benzene. In the UV-visible absorption spectrum of the polymer prepared from diethynylbenzene and mesitylborane, the peak due to π - π^* transition of the polymer backbone was observed at 399nm. From this result, it was confirmed that π -delocalization length was highly extended via the boron atom. The polymers obtained were highly fluorescent. In every case, when a dilute chloroform solution was excited at 350nm at room temperature, an intense emission was observed in a visible blue region. The polymers obtained here were very stable compared with the organoboron polymers reported previously.¹ In this hydroboration polymerization with mesitylborane, various aromatic diynes such as diethynylthiophene, furan, and pyridine could also be used to produce the corresponding π -conjugated organoboron mainchain polymers.⁷

As alternative way for the preparation of π -conjugated organoboron mainchain polymers, polycondensation between Grignard reagents and aryldimethoxyborane was carried out to give poly(phenyleneborane)s.⁸ In the resulting polymers, the higher thermal stability is expected due to the absence of a retro-hydroboration (β -elimination) process during their thermal degradation.

References Y. Chujo, *et al.*, 1) *ACS Symp. Ser.*, **572**, 398 (1994). 2) *Macromol. Symp.*, **118**, 111 (1997). 3) *Macromolecules*, **24**, 345 (1991). 4) *J. Macromol. Sci., Pure & Appl. Chem.*, **A31**, 1647 (1994). 5) *Macromolecules*, **25**, 33 (1992). 6) *J. Am. Chem. Soc.*, **120**, 5112 (1998). 7) *Macromolecules*, **32**, 4467 (1999). 8) *J. Am. Chem. Soc.*, **120**, 10766 (1998).

Dynamic and Selective Responses of Organically-Modified Silica Sol-Gels

Bakul C. Dave

*Department of Chemistry and Biochemistry
Southern Illinois University at Carbondale
Carbondale, IL 62901-4409.*

Materials that can sense signals and produce a definite dynamic response in the form of a change in shape or size offer appealing technological prospects for many applications including design of shape memory systems, drug delivery devices, chemical valves, artificial muscle mimics, and actuators. However, a rational design of active materials with predetermined responsivity still remains an elusive goal. Consequently, design of efficient response-active materials with molecularly tunable responses has been a long sought-after goal. This presentation will focus on strategies to elicit dynamic responses from silica-based materials which are prepared using the sol-gel process. For this purpose, organically-modified precursors are used to form organic-inorganic hybrid glasses. Starting from a judiciously selected molecular precursor, the sol-gel reaction yields a solid state glass—a mechanically robust yet elastic material—that is capable of generating dynamic responses when subjected to different physicochemical stimuli. The dynamic responses of these glasses to several environmental variables including pH, solvent, salts, temperature, electrical potential, metal ions, and biomolecules will be elaborated in this presentation. Conversion of different forms of physicochemical energy to mechanical energy will be shown with the sol-gel-derived materials and devices to illustrate their use as technologically compatible intelligent systems for practical applications. The use of these glasses for molecular recognition, and separation will also be discussed.

Nano-objects with controlled shape, size and composition from block copolymer – ceramic hybrid materials.

ULRICH WIESNER

Materials Science & Engineering, Cornell University, 329 Bard Hall, Ithaca, NY 14853

Currently, a great deal of attention is being paid to the synthesis of complex organic-inorganic hybrid (OIH) materials with long range order. A biomimetic approach typically employed is to use organic structures formed through self-assembly as structure directing agents. The final morphology is then determined by the cooperative organization of organic and inorganic species into three dimensionally structured arrays, a central concept also discussed in the field of biomineralization. Here the effect of

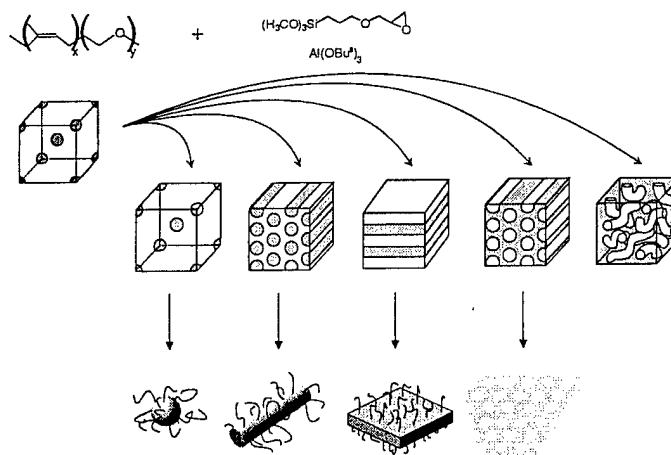


Fig.1: Concept of the preparation of nanostructured organic inorganic hybrid materials

block copolymers as structure directing agents will be discussed.[1] It will be shown that unprecedented morphology control becomes possible by changing from conventional silicon precursors to organically modified ceramic (ormocer) precursors in the block copolymer directed synthesis. From the combination of inorganic siliceous components in a hybrid material with polymers a wide range of research activities close to applications can be anticipated in the near future. First, a blend of desirable macroscopic properties (mechanical, thermal, etc.) is expected. Since the block copolymer chemistry (architecture, chain length, composition, etc.) can be varied substantially, fine-tuning of composite properties becomes possible. Furthermore, mesoporous materials with large pore sizes are accessible with possible applications in the field of separation technology (Fig.1). The resulting hybrid materials show a unique type of interface between organic and inorganic components [2] which can be employed to prepare 'hairy' nano-objects of controlled shape, size and composition (Fig.1). This opens access to nano-engineering of ceramic materials and applications in nanobiotechnology are discussed.

References

1. M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schädler, U. Wiesner. *Organically Modified Aluminosilicate Mesostructures from Block Copolymer Phases*, Science **278**, 1795 (1997).
2. S. M. De Paul, J. W. Zwanziger, R. Ulrich, U. Wiesner, H. W. Spiess, *Interface Structure of Inorganic-Block Copolymer Composites*, J. Am. Chem. Soc. **121**, 5727 (1999).

Solid-state NMR Investigation on Organically-Modified Ceramics Prepared from Alkoxysilanes

Yoshiyuki Sugahara,* Hiroshi Nakashima,* Yoshihiko Komori,* Kazuyuki Kuroda,*
and Shigenobu Hayashi**

*Department of Applied Chemistry, School of Science and Engineering,
Waseda University, Shinjuku-ku, Tokyo 169-8555 JAPAN

**National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305-8565
JAPAN

Sol-gel processing has been attracted increasing attention for the preparation of both amorphous and crystalline materials. Generally metal alkoxides are used for starting materials. Organically-modified ceramics, prepared by co-hydrolysis of metal alkoxides, have been developed recently, and are usually obtained as an amorphous materials. Thus, the structures of organically-modified ceramics should be investigated, but reported information is very limited.

Solid-state NMR is a powerful technique for investigating local environments of amorphous materials. Solid-state ^{29}Si NMR provides valuable information on amorphous materials, such as silica glass. We have applied this technique to organically-modified ceramics obtained by co-hydrolysis of alkoxysilanes.

Tetraethoxysilane (TEOS) and organotriethoxysilane ($\text{RSi}(\text{OEt})_3$, $\text{R}=\text{CH}_3$, C_5H_{11} , C_8H_{17}) were co-hydrolyzed ($\text{Alkoxysilane}:\text{H}_2\text{O}:\text{EtOH}:\text{HNO}_3=1:x:10:0.3$, $x=2, 5, 10, 20$) at ambient temperature for 1 h, and the resultant solution was aged at 60 °C. The product was further dried at 60 °C under reduced pressure. The xerogel was analyzed by ^{29}Si solid-state NMR. The ^{29}Si NMR spectra of the products exhibited signals for Q^3 ($(\text{SiO})_3\text{SiOR}'$; $\text{R}=\text{H}, \text{Et}$), Q^4 ($(\text{SiO})_4\text{Si}$), T^2 ($(\text{SiO})_2\text{Si}(\text{OR}')\text{R}$), and T^3 ($(\text{SiO})_3\text{SiR}$) environments, indicating the formation of cross-linked structures. In order to obtain further information, relaxation behavior was investigated by estimating relaxation time constants ($T_{1\rho}^{\text{H}}$ and T_{SiH}). $T_{1\rho}^{\text{H}}$ is proton spin-lattice relaxation time in a rotating frame and T_{SiH} is related to the polarization transfer (T_{SiH}^{-1} corresponds to the cross-polarization (transfer) rate). The $T_{1\rho}^{\text{H}}$ values of the T^2 , T^3 , and Q^3 environments were similar in each system, indicating sufficient ^1H spin diffusion. On the contrary, $T_{1\rho}^{\text{H}}$ of the Q^4 environment was clearly different from those of the other three environments. This appears to be ascribed to insufficient polarization transfer from proton to silicon at the Q^4 environment.

ELASTOMERS FROM DIHYDROXY-POLYDIMETHYLSILOXANE AND ALKOXY-SILANES: SURFACE MICROSTRUCTURES AND SURFACE CHARACTERIZATION.

Kenneth J. Wynne
Department of Chemical Engineering, Room 444
Virginia Commonwealth University
601 West Main Street
Richmond, VA 23284-3028
Ph: 804-828-9303
e-mail: kjwynne@vcu.edu

The research results reported are aimed at understanding the surface properties and stability of elastomers generated by the reaction of alkoxy-silanes with hydroxy-terminated PDMS macromonomers. The tributyltin diacetate catalyzed reaction of tridecafluoro(1,1,2,2, tetrahydrooctyl) triethoxysilane (FTEOS) with hydroxyl-terminated polydimethylsiloxane (PDMS) has been investigated to prepare surface-modified "self-reinforced" siloxane elastomers. Tapping Mode Atomic Force Microscopy (TM-AFM) reveals that surface phase separation occurs as a function of FTEOS concentration. For example, FTEOS-6x compositions (where 6x signifies alkoxy functionality 6 times PDMS silanol functionality) exhibited micron scale "islands" of fluorinated siliceous phase (FSP) in a siloxane-rich "sea". Dynamic Contact Angle Analysis (DCA) in water on FTEOS/FSP coatings yields complex, compositionally depended force vs. displacement curves (fdc's).

In a second effort, polydimethylsiloxane networks have been prepared utilizing poly(diethoxysiloxane) or ES40 as the alkoxy-silane crosslinker. ES40, with an approximate formula $(\text{SiO}(\text{OEt})_2)_n$, is an oligo-alkoxy-siloxane that is less volatile than tetraethyl orthosilicate (TEOS). Network formation occurs over wide ranges of stoichiometry, as alkoxy-silane in excess of that required for co-condensation with α,ω -disilanol-polydimethylsiloxane $[\text{HO}(\text{Me}_2\text{SiO})_n\text{H}]$ undergoes self-condensation producing a siliceous domain (SD). Compositions with $\text{SiOEt} / \text{SiOH}$ ratios from 4 to 30 were prepared. In designations such as "ES40-4x", the "4" denotes the initial $\text{SiOEt} / \text{SiOH}$ ratio. Solid-state ^{29}Si NMR spectroscopy was used to determine the relative amounts of $(\text{Me}_2\text{SiO})_n$ and SD. The integrated ^{29}Si NMR data was in agreement with initially measured stoichiometry. The relative amounts of Q^2 , Q^3 , and Q^4 species in the SD were estimated by deconvolution of the ^{29}Si NMR peaks. Both light microscopy and TM-AFM show that surface features are slowly generated on surfaces of PDMS-SD compositions "4x" and higher. These surface features consist of numerous "islands" of varying size. At 1 mo., PDMS/SD surface features are no larger than $\sim 1 \mu\text{m}$, whereas after 6 mos. feature size is broadly distributed up to $\sim 10 \mu\text{m}$. Differing Dynamic Contact Angle (DCA) analysis protocols with water as the interrogating fluid showed that water contamination affects force vs. distance curve (fdc) data. Intrinsic wetting behavior is reproduced only with a protocol where clean water is used for each DCA cycle. The compositionally dependent stability in water was determined. The ES40-12x composition showed the greatest resistance to mass loss in water (0.08 wt% / mo).

Zirconium-Containing Organic-Inorganic Polymer Hybrids

GUNJI Takahiro and ABE Yoshimoto

Department of Industrial Chemistry,

Faculty of Science and Technology,

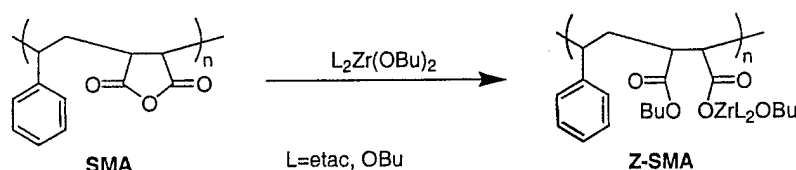
Science University of Tokyo

2641 Yamazaki, Noda, Chiba 278-8510 Japan

Tel. +81-471-24-1501 (ex. 3638) Fax. +81-471-23-9890

E-mail: gunji@ci.noda.sut.ac.jp

Organic-inorganic hybrid materials have been focused on as novel functional materials with both organic and inorganic properties. So far, the silicon-based hybrids have been energetically studied in many field, while the zirconium-containing polymer hybrids (Z-SMA) have been poorly investigated. In this talk, the preparation and applications of Z-SMA will be presented based on the reaction of zirconium alkoxides with styrene/maleic anhydride copolymer (SMA).



Z-SMA was synthesized according to the following methods A and B. **Method A:** Into a tetrahydrofuran solution of SMA, a tetrahydrofuran solution of zirconium tetrabutoxide (ZTB) or bis(ethyl acetoacetato)zirconium dibutoxide (EZB) was added dropwise. After stirring, reflux, and concentration, Z-SMA was isolated by reprecipitation. **Method B:** Into a tetrahydrofuran solution of ZTB or EZB, a tetrahydrofuran solution of SMA was added dropwise. After stirring, reflux, and concentration, Z-SMA was isolated by reprecipitation. Z-SMA bulks and gel films were prepared by aging a tetrahydrofuran solution of Z-SMA in a glass vial or a TeflonTM beaker. Z-SMA coating films were prepared by dip-coating of a 10 wt % tetrahydrofuran/methyl ethyl ketone (1/1) Z-SMA solution on a substrate. Z-SMA ceramic coating films were prepared by the pyrolysis of coating films on silicon wafer or silica glass under nitrogen atmosphere.

The reaction of SMA with ZTB or EZB was monitored by means of FT-IR spectra. The decreasing intensity of $\nu_{C=O}$ (acid anhydride) and the appearance of $\nu_{C=O}$ (carboxylate group).

Z-SMA was prepared from ZTB and SMA in the molar ratio of ZTB/SMA=0.5, 1 or 2 by method A and ZTB/SMA=1, 2, 5 or 10 by method B. The zirconium content of Z-SMA by method B was greater than that of method A. On the other hand, Z-SMA was synthesized from EZB and SMA in the molar ratio of EZB/SMA=0.5-10 by method B.

Molecular weight (M_n) of Z-SMA was 2490 (ZTB and SMA) or 1410 – 1580 (EZB and SMA). The former suggests the cross-linking between SMA molecules by a zirconium atom. Z-SMA bulks and gel films containing zirconium of ca. 5–20% (film thickness: 0.1–0.3 mm) were prepared by aging the Z-SMA solution for 5-14 days. These bulks and gel films were homogeneous, transparent and crack-free.

Z-SMA coating films with thickness of submicron level were prepared by coating on the organic polymer, metal, ceramics and glass substrates. With increasing zirconium content, the transmittance of the coating films decreased, while the adhesive strength, pencil-hardness and refractive index of the coating films increased.

Z-SMA ceramic coating films were thermally stable on heating to 1000°C. The hardness and refractive index of the coating films increased with increasing pyrolysis temperature. The refractive index of the films was close to the value of ZrO_2 at 500°C. The transmittance of the films once decreased at 500°C and increased at 800°C. These results suggest that the coating films were densified and finally ZrO_2 films were prepared by the combustion and elimination of organic groups.

Mesomorphic Phase Transition in Organophosphazenes

Keiichi Moriya

Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido, Gifu 501-1193, JAPAN

Liquid crystalline organophosphazenes including polymers and trimers have been synthesized extensively.¹⁻⁵ Their features are in the long spacers between mesogens and phosphazene nucleus. Therefore, we have synthesized several phosphazene compounds by the introduction of mesogenic side chains directly into the phosphorus atoms.⁶⁻¹⁰

In this study several organophosphazenes which consist of trimers, tetramers and polymers were synthesized and their phase transitions were investigated by thermal, optical and spectroscopic methods. Especially the effects of the difference in the phosphazene nucleus on the phase transitions were of great interest. The organophosphazenes described are shown in Figure 1.

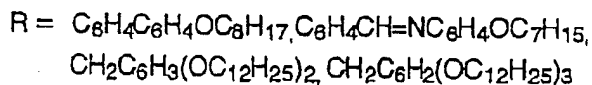
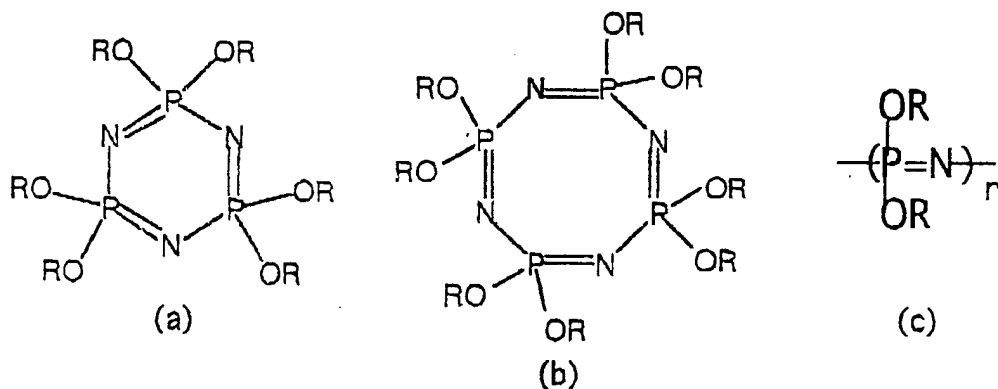


Figure 1. Organophosphazenes of several mesogenic side chains.

Experiments

The cyclotriphosphazenes, cyclotetraphosphazenes and polyphosphazenes were synthesized from corresponding chlorosubstituted phosphazenes, mesogenic alcohol and sodium hydride. Polydichlorophosphazene was synthesized by ring-opening polymerization of the hexachlorocyclotriphosphazene. The trimers and tetramers were purified by recrystallization. Polymers were purified by reprecipitation of the polymers

into heptane. The compounds were confirmed by ^{31}P and ^1H NMR, IR and elemental analyses. The phase transitions were studied by DSC measurements. The textures of the compounds were observed by polarizing microscope observations. The liquid crystalline phase was confirmed by the X-ray diffraction.

Discussions

For the octyloxybiphenyl side chains, the trimers have mesomorphic transitions, but the tetramers do not have mesomorphic transitions, which was explained by the difference of the crystal structures of the trimers and tetramers. In the crystal phase of trimers with biphenoxy side chains each three side chains situate upwards and downwards perpendicular to the cyclotriphosphazene ring and this molecular structure helps the formation of the smectic layer structure. The molecular structure of the trimer with octyloxybiphenyl groups was estimated assuming all-trans conformation for the crystal structure of hexakisbiphenoxycyclotriphosphazene.¹¹ However, in the tetramers with octyloxybiphenoxy side chains, the rings are not in the same plane and the side chains point relatively random directions. In the polyphosphazenes with octyloxybiphenoxy groups, no mesomorphic phase was observed.

In the organophosphazenes with Schiff's base moiety, the situation is a little different from above. All the trimers, tetramers and polymers with Schiff's base have mesophases. The mesogenicity in organophosphazenes with Schiff's base moiety is much higher than that with biphenoxy groups. Probably, the polarity in Schiff's base helps the stability of the mesomorphic phase.

References

1. C. Kim and H. R. Allcock, *Macromolecules*, 1987, 20, 1726.
2. R. E. Singler, R. A. Willingham, R. W. Lenz, A. Furukawa and H. Finkelmann, *Macromolecules*, 1987, 20, 1727.
3. H. R. Allcock and C. Kim, *Macromolecules*, 1989, 22, 2596.
4. H. R. Allcock and C. Kim, *Macromolecules*, 1990, 23, 3881.
5. H. R. Allcock and E. H. Klingenberg, *Macromolecules*, 1995, 28, 4351.
6. A. M. Levelut and K. Moriya, *Liq. Cryst.*, 1996, 20, 119.
7. K. Moriya, H. Mizusaki, M. Kato, T. Suzuki, S. Yano, M. Kajiwara and K. Tashiro, *Chem. Mater.*, 1997, 9, 255.
8. K. Moriya, T. Suzuki, H. Mizusaki, S. Yano and M. Kajiwara, *Chem. Lett.*, 1997, 1001.
9. K. Moriya, T. Masuda, T. Suzuki, S. Yano and M. Kajiwara, *Mol. Cryst. Liq. Cryst.*, 1998, 318, 267.
10. K. Moriya, T. Suzuki, Y. Kawanishi, T. Masuda, H. Mizusaki, S. Nakagawa, H. Ikematsu, K. Mizuno, S. Yano and M. Kajiwara, *Appl. Organometal. Chem.*, 1998, 12, 771.
11. H. R. Allcock, D. C. Ngo, M. Parvez, R. R. Whittle and W. J. Birdsall, *J. Am. Chem. Soc.*, 1991, 113, 2628.

Mesoscopic Structure of Polymer-Inorganic Nanocomposites: Impact on Chain Behavior and Physical Properties

Richard A. Vaia

Air Force Research Laboratory, Polymer Branch, Wright-Patterson AFB, Dayton, OH
45433-7750

Over the last decade, the utility of inorganic nanoparticles as additives to enhance polymer performance has been established. Notwithstanding these accomplishments, an understanding of the fundamental correlation between nano (1-100 nm) and mesoscale (100-1000 nm) structure and ultimate physical, mechanical and thermal properties have only been tentatively examined for a few specific systems, without the possibility for any broad predictive guidelines being discernible. As with other multiphase systems exhibiting nano (1-100 nm) and meso (100-500 nm) order (such as biopolymers, block-copolymers, colloidal suspensions, liquid crystals), physical properties ranging from toughness to optical clarity are determined by morphology on various lengthscales which in turn is dependent on everything from process history to specific polymer-inorganic interactions. Additionally, because of the morphological length scales, the exceedingly large interfacial area between constituents results in the volume fraction of interfacial regions approaching one! Thus physical properties are dominated by the properties of these interfacial regions and understanding chain behavior (conformation, relaxation, crystallization) in these regions is paramount to understanding these nanocomposites.

This presentation will discuss two current efforts to understand the impact of nanoscale and mesoscale distribution of inorganic on the ultimate physical properties of nanocomposites. First, in contrast to conventional wisdom that addition of the inorganic phase is for reinforcement, the nanoscale dispersion affords the opportunity to utilize the ultrafine particles as precursors to form passivation coatings on the materials surface in response to aggressive environments. Optimization of the size and spatial distribution of the inorganic constituent significantly increases the char's resistance to oxidation and mechanical erosion in an ablative environment resulting in a new class of ablatives with performance rivaling current state-of-the-art options. Second, the impact of phase distribution and polymer-silicate interactions on crystallization of poly(caprolactam) (nylon 6) will be discussed. In addition to a change in crystal form (g v. a), the presence of the layers substantially alters nucleation rate and growth kinetics. These observations are attributed to the layers disrupting the crystal lamellae organization. Control of these processes is critical to process optimization of the properties of these semi-crystalline polymer nanocomposites. These studies are portions of our general program to establish a fundamental understanding of the influence of nanoscopic constituents and their hierarchical morphology on bulk mechanical, electrical and optical properties.

An Efficient Encapsulation of Colloidal Silica by Emulsion Polymerization of Acrylates. A Facile Simple Approach to Obtain Hybrid Materials with Controlled Properties.

Tsutomu Mizutani, Kohji Murata, Kohji Arai, Masatoshi Miyamoto, and Yoshiharu Kimura

*Department of Polymer Science and Engineering, Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto 606-8585, JAPAN*

Latex particles have been widely used as water-borne coatings. Until now, various particle structures and morphologies have been devised for the purpose of functionalization of the coatings, including core-shell, microdomain, and void structures. The use of hybrid emulsions involving such inorganic particles as colloidal silica has also convinced of one of the simplest methods to obtain inorganic/organic hybrid coatings and films. A typical example is the blending of acrylic emulsion with colloidal silica, although the easy aggregation behavior of the latter composition often limits the inorganic content in the blends. Another attempt is the synthesis of surface-modified silica particles in order to intensify the inorganic-organic interaction and to allow the encapsulation of the silica particles with polymeric materials. However, the direct surface modification of the silica particles is not easily conducted in a manufacturing scale. In the present study, we report on an efficient method for obtaining hybrid particles encapsulating the colloidal silica by the emulsion polymerization technique and their formation of a stable inorganic/organic hybrid coat that has never been attained before.

Typically, a small amount (5 g) of an acrylic monomer mixture (MMA/BA/MAA = 49/50/1 in wt%) was subjected to the seed polymerization at 70 °C in the presence of colloidal silica (Nissan Chemicals Snowtex ST-50; 50 wt% solid content, 200 g) with a nonionic emulsifier (Adeka NE-10; 3 g) having a low clouding point (40 °C) and a cationic initiator. Then, the ordinary emulsion polymerization of the monomer mixture (95 g) was continued with an anionic emulsifier (SDS: Kao Emulgen 840S; 2 g) and an ordinary initiator. The resultant emulsion was cast on a glass plate to form a coating film. The acrylates/silica ratio was 100/100 (in wt%) in this case.

The emulsifier used in the seed polymerization was allowed to deposit on the surface of the silica particles when the polymerization system was heated above the clouding point of the emulsifier. The surface of the particles served as the primary site for the polymerization of the monomer supplied from the serum phase of the emulsion, and the copolymerization with the emulsifier stabilized the surface coat. This polymer coat once formed became the polymerization site for the charged monomers in the following emulsion polymerization to form the stable hybrid particles encapsulating silica colloids in the center. The casting of the hybrid emulsion gave a transparent film having higher hardness and fire-resistibility depending on the silica contents. The content of the silica particles being desirable to obtain a stable coating ranged from 0.5 to 3 times relative to that of the polyacrylates in the hybrid particles, whereas the highest content remained 1.5 times in the simple particle blends. The characteristic properties of the hybrid particles and coatings will be reported in detail.

PREPARATION OF ORGANICALLY MODIFIED LAYERED SILICATES

Kazuyuki KURODA

Department of Applied Chemistry and Kagami Memorial Laboratory for Materials
Science & Technology, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

The interactions between layered silicates and organic species produce various unique materials. By choosing appropriate layered silicates, the structural control of guest species or the host materials has been accomplished.

The advantage of the use of layered materials is its confinement of guest species in their two-dimensional spaces to induce selective orientation. Kaolinite, a 1:1 type of clay mineral, is unique because the interlayer region is sandwiched between hydroxyl groups of $\text{AlO}_2(\text{OH})_2$ sheets in one side and oxide arrangements of silicate sheets in the other, affording an asymmetric nanoenvironment. Such an environment is expected to be a unique medium for organizing guest molecules. The orientation of organic guest species induced simply by the interlayer surface structures is noteworthy. By using a guest displacement method a kaolinite-*p*NA intercalation compound where *p*NA molecules were aligned in one direction between the layers was successfully formed.

Layered polysilicates such as magadiite, octosilicate (ilerite), and kanemite can be regarded as two-dimensional inorganic polymers and their organically modified derivatives are inorganic-organic macromolecular hybrids. Layered polysilicates possess silanol groups on the interlayer surfaces of the silicate sheets and the groups can be used to prepare organically modified layered silicates. Bulky silyl groups such as alkyldimethylsilyl groups can be grafted onto the interlayer surfaces of these layered polysilicates.

A layered polysilicate, kanemite, is composed of single layered silicate sheets and a structural transformation on intercalation of organoammonium ions was reported by us. Since the discovery of the formation of mesoporous silica derived from kanemite, various mesoporous silicas have been synthesized. Novel mesoporous silica with lozenge one-dimensional channels derived from kanemite was formed, which cannot be derived by the reported cooperation of surfactants and soluble silica sources. Intralayer condensation and the bending of the silicate sheets were clearly observed.

INTERPHASE STRUCTURE AND DYNAMICS IN POLYMER NANOCOMPOSITES

Emmanuel P. Giannelis

Materials Science Engineering and Cornell Center for Materials Research
Cornell University

Polymer nanocomposites, especially polymer-layer silicate nanocomposites, represent a radical alternative to conventional polymer composites. Because of their nanometer phase dimensions the nanocomposites exhibit properties dramatically different from their micron-scale counterparts. These include enhanced mechanical properties, decreased gas permeability, increased solvent resistance and decreased flammability.

Even though a significant progress has been made in developing different nanocomposites an understanding has yet to emerge. A major challenge in developing nanocomposites for systems ranging from high performance to commodity polymers is the lack of even simple structure/properties models. In the absence of such models progress in nanocomposites has remained largely empirical. Similarly, predicting the ultimate material limits or maximum performance for different classes of nanocomposites is almost impossible at present.

Can nanocomposites be adequately modeled by extrapolating what is already known for conventional polymer composites and taking into account their larger interphase fraction because of nanodispersion and the much higher surface area available? The quandary of such an approach is that in the nanocomposites the interphase is much thinner from the corresponding conventional composites. Specifically in nanocomposites polymer chains are confined at distances ranging from about the statistical segment length to the radius of gyration of the polymer. Little is known about the properties of polymers confined in such a severe (from less than $\sim 1 - 15$ nm), almost two-dimensional environment.

In this presentation I will review our work on the interphase structure and dynamics in nanocomposites by combining both experimental and computer modeling studies.

SHORT
BIOGRAPHIES
OF
PARTICIPANTS

Yoshimoto Abe

Professor

Department of Industrial Chemistry, Faculty of Science and Technology,
Science University of Tokyo, 2641 Yamazaki, Noda, Chiba 278-8510, Japan

Phone +81+471+24+1501(ex 3608), Fax +81+471+23+9890

e-mail abeyoshi@ci.noda.sut.ac.jp

PERSONAL

Date of Birth : September 6, 1940

Family : Married (two Sons)

Home : 1411-6 Yamazaki, Noda, Chiba 278-0022, Japan

Phone : +81+471+24+9741

EDUCATION

1964 B.S. Applied Chemistry, Science University of Tokyo

1966 M.S. Chemistry, Science University of Tokyo

1971 Ph.D. Chemistry, Science University of Tokyo

PERSONAL APPPOINTMENTS

1969 Research Associate, Department of Industrial Chemistry,
Faculty of Science & Technology, Science University of Tokyo

1975 Assistant Professor

1976 Visiting Scientist, Polymer Division, University of Florida (~1977)

1980 Associate Prof.

1989 Professor (Chair professor, ~ 1991, 1997~1999)

1999~ Vice Student Dean of Science University of Tokyo (Student Dean of Noda Campus)

MEMBERS

The Chemical society of Japan, The Society of Polymer Science, Japan,

The Japan Society of Color Material, The Ceramic Society of Japan

American Chemical Society

AWARDS

The award of the paper " Synthesis and Properties of Metal IV Chelate Complexes as Coloring

Materials " (The Japan Society of Color Material)

RESEARCH INTERESTS

Metal Alkoxides and Chelates, Siloxane Oligomers and Polymers

Metalloxane Monomers and Polymers, Inorganic Polymers and Hybrids, Ceramics

BIOGRAPHICAL SKETCH

Harry R. Allcock

Evan Pugh Professor of Chemistry
The Pennsylvania State University, University Park, PA 16802

Personal Data, Education, and Positions Held

Birthplace, England; Citizenship, U.S.A.

University of London, B.Sc. 1953, in Chemistry

University of London, Ph.D. 1956, in Organometallic Chemistry

Purdue University, Postdoctoral Fellow, 1956-1957, Synthetic Organic and Inorganic Chemistry

National Research Council of Canada, Ottawa, Postdoctoral Fellow, 1958-1960, Polymer Chemistry

American Cyanamid Company, Stamford, Connecticut, Research Scientist and Senior Research Scientist, 1961-1966, Inorganic Chemistry and Polymer Chemistry

The Pennsylvania State University, University Park, Associate Professor of Chemistry (1966-70), Professor (1970-85), and Evan Pugh Professor (1985-); Board member of the Penn State Materials Research Institute (1991-1998); Member of the Biotechnology Institute (1986-); Member of the Advisory Board, Department of Bioengineering (1989-)

Research Interests and Accomplishments

Design, synthesis, and properties of new polymers, with a special emphasis on advanced hybrid materials.

Honors

American Chemical Society National Award in Polymer Chemistry, 1984; Guggenheim Fellow, 1986/1987; Chemical Pioneer Award of the American Institute of Chemists, 1989; American Chemical Society National Award in Materials Chemistry, 1992; American Chemical Society Herman Mark Award, 1994. Visiting scientist at Stanford University (1975), Imperial College of Science and Technology, London (1976), and the Almaden Laboratories of IBM in San Jose (1987). Membership at different times on 10 editorial boards.

Books

(a) *Single author monographs.* "Heteroatom Ring Systems and Polymers", Academic Press, 1967 (401 pages). "Phosphorus-Nitrogen Compounds - Cyclic, Linear, and High Polymeric Systems", Academic Press, 1972, (498 pages). (b) *Co-authored Books.* "Contemporary Polymer Chemistry" by H. R. Allcock and F. W. Lampe. Prentice Hall, 1st edition 1981, 2nd edition 1990 (624 pages). "Inorganic Polymers" by J. E. Mark, H. R. Allcock, and R. West, Prentice Hall, 1992 (272 pages). (c) *Edited volumes.* "Inorganic and Organometallic Polymers" edited by M. Zeldin, K. J. Wynne, and H. R. Allcock, American Chemical Society Symposium Series 360, 1988 (512 pages). "Inorganic and Organometallic Polymers II; Advanced Materials and Intermediates" edited by P. Wisian-Neilson, K. J. Wynne, and H. R. Allcock, American

Chemical Society Symposium Series 572, 1994 (536 pages). "Inorganic Syntheses, Vol 25", H. R. Allcock, Editor in Chief, Wiley-Interscience, 1989, (300 pages).

Research Publications and Invited Lectures

More than 400 research publications, 47 issued patents, and 390 invited lectures in the U.S. and abroad including 12 at Gordon Research Conferences, and numerous endowed lectures.

Yoshiki CHUJO

Professor

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University

Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Phone: +81-75-753-5655 FAX: +81-75-753-5675

e-mail: chujo@chujo.synchem.kyoto-u.ac.jp

PERSONAL

Date of Birth: April 4, 1952
Family: Married (one Daughter)
Home: 2 Nishitsutamachi, Kitashirakawa, Sakyo-ku, Kyoto 606-8261, Japan
Phone: +81-75-711-6486

EDUCATION

1975 B.S., Synthetic Chemistry, Kyoto University
1977 M.S., Synthetic Chemistry, Kyoto University
1980 Ph.D., Synthetic Chemistry, Kyoto University

PROFESSIONAL APPOINTMENTS

1980 Postdoctoral Fellow (Japan Society for the Promotion of Science),
Department of Synthetic Chemistry, Kyoto University
1981-86 Research Associate, Department of Synthetic Chemistry, Nagoya University
1982-83 Visiting Scientist, Department of Chemistry, Virginia Polytechnic Institute and State University
1986-93 Lecturer, Department of Synthetic Chemistry, Kyoto University
1993-94 Lecturer, Department of Polymer Chemistry, Kyoto University
1994-95 Associate Professor, Department of Polymer Chemistry, Kyoto University
1995-Present Professor, Department of Polymer Chemistry, Kyoto University
1997-98 Visiting Professor, University of Rennes I, France

EDITORIAL ACTIVITIES

1991-93 Kobunshi Ronbunshu (Japanese Journal of Polymer Science and Technology)
1994-96 Kaigai Kobunshi Kenkyu (Current Polymer Research)
1996-98 Nippon Kagaku Kaishi
1996- Polymer Bulletin
1996- Nippon Secchaku Gakkaishi (Journal of Adhesion Society, Japan)
1999- Bulletin of the Chemical Society of Japan
1999- Journal of Inorganic and Organometallic Polymers
1999- Polymer Journal

MEMBERS

The Society of Polymer Science, Japan
The Chemical Society of Japan
American Chemical Society
The Royal Society of Chemistry
The Society of Synthetic Organic Chemistry, Japan
Materials Research Society of Japan
The Adhesion Society of Japan
The Rubber Society of Japan
Kinki Chemical Society

AWARDS

1986 The Award for Encouragement of Research in Polymer Science, the Society of Polymer Science, Japan
1991 The Award of the Society of Polymer Science, Japan

RESEARCH INTERESTS

Polymer Synthesis
New Polymerization Reactions
Reactive Polymers
Inorganic Polymers

BAKUL C. DAVE

I. EDUCATION.

- Ph. D.** Department of Chemistry. University of Houston. 1989-1993.
M.Sc. Department of Chemistry. Indian Institute of Technology, Bombay. 1987-1989.
B.Sc. Department of Chemistry. Institute of Science, University of Bombay, Bombay. 1984-1987.

II. PROFESSIONAL EXPERIENCE.

- Assistant Professor** (Aug., 1996-).
Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, IL 62901.
Research Associate (1994-1996).
Department of Chemistry and Biochemistry, and Department of Materials Science and Engineering, University of California, Los Angeles, CA 90095. (1994-1996).
Graduate Research Assistant (1989-1994).
Department of Chemistry. University of Houston, Houston, TX 77204.
Undergraduate Research Aide (1987-1989).
Department of Chemistry. Indian Institute of Technology, Bombay, India.

III. RESEARCH.

Research Interests and Specialties.

Materials Chemistry, Bioinorganic Chemistry, Spectroscopy.
Synthesis of Novel Materials. Design and Assembly of Integrated Nanostructures. Molecular Electronics and Photonics. Molecule-Based Devices. Biomaterials. Design of Intelligent Systems.

Research Grants Received.

- (1) Start up Grant. Department of Chemistry and Biochemistry, Southern Illinois University, \$ 180,000 for 2 years.
- (2) "Bioactive Smart Materials" Materials Technology Center at Southern Illinois University; \$19, 980 for 1 year beginning Nov. 1996.
- (3) "Design and Assembly of Novel Materials and Devices based on Integration of Biomolecules in SnO₂ Sol-Gels" Special Research Grant Award Program of the Office of Research Development and Administration (ORDA), SIUC; \$20,000.
- (4) "Design and Assembly of Novel Materials and Devices based on Integration of Biological Molecules in SnO₂ Sol-Gels" Oak Ridge Associated Universities' Junior Faculty Enhancement Award, \$5,000.
- (5) "Designer Biomaterials" Materials Chemistry Initiative, MTC, SIU. \$20090.
- (6) "Smart Glasses" Materials Chemistry Initiative, MTC, SIU. \$20090.

IV. RECENT PUBLICATIONS.

1. "Enzymatic Conversion of Carbon Dioxide to Methanol: Enhanced Methanol Production in Silica Sol-Gel Matrices" R. Obert, and B. C. Dave *J. Am. Chem. Soc.* **1999**, *121*, 12192.
2. "Synthesis of Sol-Gel Encapsulated Heme Proteins with Chemical Sensing Properties" E. H. Lan, B. C. Dave, J. M. Fukuto, B. Dunn, J. I. Zink, and J. S. Valentine *J. Chem. Mater.* **1999**, *9*, 45.
3. "Smart Glasses Designed to Generate Dynamic Responses" *Mater. Tech.* **1999**, *14*, 115.
4. "Bioelectronic Glasses: Electrical Addressability of Sol-Gel Immobilized Biomolecules" Y. Tang, and B. C. Dave *Adv. Mater.* **1998**, *10*, 1536.
5. "Selective Intake and Release of Proteins by Organically-Modified Silica Sol-Gels" M. S. Rao, and B. C. Dave *J. Am. Chem. Soc.* **1998**, *120*, 13270.
6. "Synthesis and Physical Properties of Polypyrrole - Vanadium Oxide Hybrid Aerogels" J. Harreld, H. P. Wong, B. C. Dave, and B. Dunn. *J. Noncryst. Solids* **1998**, *225*, 319.
7. "Sol-Gel Matrices for Protein Entrapment" B. C. Dave, B. Dunn, J. S. Valentine, and J. I. Zink. *Immobilized Biomolecules in Analysis: A Practical Approach*, F. S. Ligler, and A. E. G. Cass (eds.), Oxford University Press, **1998**, 113-134.
8. "Strategies for Encapsulating Biomolecules in Sol-gel Matrices" B. Dunn, J. M. Miller, B. C. Dave, J. S. Valentine, and J. I. Zink *Acta Mater.* **1998**, *46*, 737.
9. "Synthesis of Protein-Doped Sol-Gel SiO₂ Thin Films: Evidence for Rotational Mobility of Encapsulated Cytochrome c" B. C. Dave, H. Soye, J. M. Miller, B. Dunn, J. S. Valentine, and J. I. Zink *Chem. Mater.* **1995**, *7*, 1431.
10. "Sol-Gel Encapsulation Methods for Biosensors" B. C. Dave, B. Dunn, J. S. Valentine, and J. I. Zink *Anal. Chem.* **1994**, *66*, 1120A.

EMMANUEL P. GIANNELIS
Department of Materials Science & Engineering
Cornell University

Education:

Ph.D., Inorganic Chemistry, 1985
Michigan State University

B.S., Chemistry, 1980
University of Athens, Athens, Greece

Positions:

1999 – Present	Professor, Materials Science & Engineering, Cornell University
2000 – Present	Affiliated Scientist, Polymer Group, IESL, Greece
1995 – Present	Member, Field of Chemical Engineering, Cornell University
1997 – Present	Member, Field of Chemistry, Cornell University
1996 - Present	Associate Director, Electronic Packaging Program
1993 – 1999	Associate Professor, Materials Science & Engr., Cornell University
1/95 - 3/95	Visiting Scientist Materials Department, University of California-Santa Barbara
1987 - 1993	Assistant Professor, Materials Science & Engr., Cornell University
1986 - 1987	Research Associate, Dépt. Chem. Engr. Michigan State University
1985 - 1986	Research Associate, Dept. of Chemistry, Michigan State University

Awards and Honors:

1999 *PEL Associates Award* in Applied Polymer Chemistry
1994 *Dean's Prize* for Excellence in Teaching
1999-Present Editorial Board, *Macromolecules*
1993-1996 Editorial Board, *Chemistry of Materials*

Professional Societies:

Sigma Xi, American Chemical Society, American Ceramic Society, Materials Research Society, Clay Minerals Society, AAAS

Research Interests:

Polymer Nanocomposites; Polymers in Confinement; Nanocomposite Electrolytes; Bio-relevant Nanocomposites; Materials for Electronic Packaging.

Other Activities

Teaching @ Cornell

ENGRI 111 - Materials by Design (Introduction to Materials Science and Engineering)
MSE 222 - Materials Chemistry
MSE 414/514 - Chemical Processing of Ceramics
MSE 447 - Materials Design Concepts I

Departmental Committees

Safety Committee, 1988-present (Chair 1996-present)
Chair, MSE Colloquium, 1990-1996
Faculty Search Committee, 1996
MSE Director Search Committee, 1997
Chair, Polymer Search Committee, 1998
Coordinator MSE Masters of Engineering Program, 1997-present

College of Engineering

Academic Standards Petitions and Credit, 1989-1991
College Safety Committee, 1998-present
Ad Hoc Tenure Committee, 1998

University Committees

CCMR (MSC) Executive Committee, Member Engineering at Large, 1995-present
Faculty Council of Representatives, 1992-1995

National/International

Co-organizer, Symposium on "Inorganic-Organic Hybrid Materials, ACS Meeting, 1996
Co-organizer, Symposium on "Organic-Inorganic Hybrids, MRS Meeting, 1998
Lecturer, Graduate Program on "Polymer Science and Applications", Greece, 1998-2000
Co-organizer, Symposium on "Organic-Inorganic Hybrids, MRS Meeting, 2000
Co-Organizer, Symposium on "Polymer Nanocomposites", ACS Meeting, 2000
Co-organizer, US-Japan Meeting on Macromolecular Hybrids, 2000

Curriculum Vitae of Dr. GUNJI Takahiro

Name: GUNJI, Takahiro

Affiliation: Research Associate of the Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo

Address: 2641 Yamazaki, Noda, Chiba 278-8510 Japan

Telephone: +81-471-24-1501 ex. 3638

Fax: +81-471-23-9890

E-mail: gunji@ci.noda.sut.ac.jp

Date of Birth: September 3, 1964

Gender: Male

Educational Background:

1983-1987 Undergraduate School of the Department of Industrial Chemistry,
Faculty of Science and Technology, Science University of Tokyo.

1987-1989 Master Course, Graduated School of the Department of Industrial Chemistry,
Faculty of Science and Technology, Science University of Tokyo.

1989-1992 Ph. D. Course, Graduated School of the Department of Industrial Chemistry,
Faculty of Science and Technology, Science University of Tokyo.

1992 Obtained Ph. D. Degree.

Work Experience:

1992-1993 Postdoctoral fellow of Bob West group, Chemistry Department, University of Wisconsin-Madison.

1993-1998 Research Assistant, the Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo.

1998-Present Assistant Professor, the Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo.

Research Interests: Inorganic polymer chemistry. Organometallic chemistry.

Personal Interests: Driving. Travel. Downhill skiing. Walking. Archeology.

April 16, 2000

Isao Hasegawa

Department of Chemistry, Faculty of Engineering, Gifu University
Yanagido 1-1, Gifu-City, Gifu 501-1193, Japan

Academic Degrees and Educational Background:

- 1980-1984 Bachelor of Engineering, Department of Applied Chemistry, School of Science and Engineering, Waseda University, Tokyo, Japan
- 1984-1986 Master of Engineering, Department of Applied Chemistry, School of Science and Engineering, Waseda University, Tokyo, Japan
- 1986-1989 Doctor of Engineering, Division of Molecular Engineering, Faculty of Engineering, Kyoto University, Kyoto, Japan

Professional/Research Experience:

- 1989 Researcher, Institute for Chemical Research, Kyoto University, Kyoto, Japan
- 1989-1991 Special Researcher, Institute of Physical and Chemical Research, Saitama, Japan
- 1991- Research Associate, Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan
- 1999- Research Advisor, Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany

Research Interests

Major research areas for the Hasegawa group include the structure control of silicate species and the synthesis and processing of inorganic polymers and organic-inorganic hybrids. Polymerization of silicate anions or hydrolysis product of tetraethoxysilane is controlled to form cage-like silicate species selectively when an adequate amount of organic quaternary ammonium ions is present together. The polymers and hybrids are prepared using the sphaerosilicate species as a starting material. The object of the polymer and hybrid synthesis is to build up controlled higher-order structures consisting of the sphaerosilicate structure as the building block. Another type of hybrids is prepared by a sol-gel reaction using an organic compound which gives a considerable amount of carbonaceous residue upon pyrolysis. The hybrids are applied as precursors for carbide and nitride ceramics which form by carbothermal reduction in an Ar and a N₂ flow, respectively. The hybrids can be processed into the fiber form, with which carbide or nitride fibers can be produced.

Scientific and Professional Societies:

- American Chemical Society
 - Division of Colloid and Surface Chemistry
 - Division of Inorganic Chemistry
 - Division of Polymer Chemistry
- Ceramic Society of Japan
- Chemical Society of Japan
- Materials Research Society
- New York Academy of Sciences
- Planetary Society
- Society of Polymer Science, Japan

Leonard V. INTERRANTE

Professor, Department of Chemistry

Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Phone: 1-518-276-8752 FAX: 1-518-276-2636; e-mail: interl@rpi.edu

EDUCATION

- 1960 B.A., Chemistry, University of California, Riverside
- 1964 Ph.D., Inorganic Chemistry, University of Illinois, Urbana

PROFESSIONAL APPOINTMENTS

- 1963-4 National Science Foundation Postdoctoral Fellow, University College London
- 1964-68 Assistant Professor, University of California, Berkeley
- 1968-85 Research Scientist, General Electric Corp. Res. & Devel., Schenectady, NY
- 1985- Professor of Chemistry, Rensselaer Polytechnic Institute

PROFESSIONAL SERVICE

- 1989-Editor, American Chemical Society journal, *Chemistry of Materials*
- 1999elected member of the Inorganic Division Committee of the IUPAC
- 1999 Selected as Materials Science Editor for the 3rd edition of the Academic Press "Encyclopedia of Physical Science and Technology"
- 1998 co-editor, "Chemistry of Advanced Materials – An Overview", Wiley-VCH
- 1996- Member, Advisory Board, International Conferences on Organosilicon Chemistry
- 1991-7 Member, Technical Advisory Board, University of Texas, NSF Science and Technology Center on Synthesis, Growth, and Analysis of Electronic Materials
- 1996- Member, International Advisory Board, Materials Research Society of India
- 1995 co-editor (with D. Murphy), *Inorganic Syntheses*, Vol. 30, "Synthesis of Non-molecular Inorganic Solids"
- 1992 Co-chair, Symposium on "Materials Chemistry - An Emerging Subdiscipline", Division of Industrial and Engineering Chemistry, ACS; ACS National Meeting, Washington, D.C. (co-editor, ACS Advances in Chemistry Series Volume

No.245)

- 1992 Panel Member, Triennial Oversight Review, Chemistry Division, NSF, Wash., DC
- 1992 Member, NSF Panel on Educational Issues in Materials Science, Chicago, IL
- 1991 Co-editor (with K.F. Jensen, L.H. Dubois and M.E. Gross), *Mats. Res. Soc. Sympos. Proc.*, Vol. 204, "Chemical Perspectives of Microelectronic Materials II"
- 1985 Chairman, and originator of the first Gordon Research Conference on "The Chemistry of Electronic Materials", Santa Barbara, CA
- 1976 Chairman, Gordon Research Conference on Inorganic Chemistry
- 1973-82 Program Chair (73-75); Secretary-Treasurer (78-80); Chair (82): Division of Inorganic Chemistry, ACS

AWARDS

- 1992 17th Waite Philip Fishel Lecturer, Vanderbilt University
- 1991 3M Lecturer in Solid State Chemistry, Univ. of British Columbia, Vancouver, CA
- 1983 Toisieme Cycle Lecturer, Universities of Berne, Fribourg and Lausanne
- 1981 Almquist Lecturer, University of Idaho
- 1980 Fellow of the American Association for the Advancement of Science

1979

Vernon Lecturer: Northeastern University

RESEARCH INTERESTS

Publications: 167 papers, 5 books, 7 patents

Inorganic and Materials Chemistry

Synthesis and properties of (Si-based) inorganic polymers; design, synthesis and application of molecular and macromolecular precursors to inorganic solids (AlN, SiC, SiO_xC_y, etc.); organic/inorganic materials; CVD with designed molecular precursors

Meisetsu Kajiwara

Dr. Professor

Department of Dental Materials Science, School of Dentistry, Aichi-Gakuin University,
1-100, Kusumoto-cho, Chikusa-ku, Nagoya 464-0814, Japan

Birthplace: Hokkaido, Sapporo
Home: 117 Nishiyamadai, Meito-ku, Nagoya 465-0071, Japan
TEL&FAX +81-52-702-2013

Degrees: 1961 B.S. Hokkaido University
1971 Dr., Ph. D., Nagoya University
Positions held: 1961 Assistant professor, Hokkaido university
1966 Associate Professor, Tomakomai Technical Collge
1967 Assistant professor, Nagoya University
1981 Visiting Scientist, MacGill Univeristy
1990 Associate professor, Nagoya University
1997 Professor, Aichi-Gakuin Univeristy
Honors: 1971 Tokai Chemical Engineeruig Award

Research Interests:

Design, synthesis and properties of inorganic polymers and oligomers.
Advanced ceramic materials using precursors
Inorganic-organic hybrid materials
Dental materials,
Lithium battery materials

Primary research publications, review articles and invited lectures:

Over 130 research publications, over 58 patents, over 200 invited lectures in Japan and abroad

Books: Synthesis and Applications of Phosphazene Compounds (1986)
Application of Inorganic Polymers (1990)
Inorganic Polymers [I] (1992)
Inorganic Polymers [II] (1993). Over 28 books.

YOSHIHARU KIMURA

Kyoto Institute of Technology
Department of Polymer Science and Engineering
Matsugasaki, Kyoto 606-8585, JAPAN

Phone: (075) 724-7804 Fax: (075) 712-3956 E-mail: ykimura@ipc.kit.ac.jp

PERSONAL

Born: August 8, 1948, in Japan
Home: 1126-1 Takakai-cho, Omihachiman, Shiga 523-0891, Japan
TEL/FAX: (0748)37-7305

EDUCATION

1971 B.S., Kyoto University
1973 M.S., Kyoto University
1976 Ph.D., Kyoto University

PROFESSIONAL APPOINTMENTS

1976-77 Post-doctoral Fellow, University of Iowa and
Colorado State University (Late Professor J. K. Stille)
1978-79 Researcher, Kyoto University
1979-81 Assistant Professor, Shiga Prefectural Junior College
1981-85 Assistant Professor, Kyoto Institute of Technology
1985-90 Associate Professor
1990- Professor
2000- Director, Cooperative Research Center of KIT

RESERACH INTERESTS

1. Inorganic polymers and ceramic fibers
2. Biodegradable polymers and biomedical materials
3. Polyimide-based materials

AWARDS

1998 The Award of the Society of Fiber Science and Technology, Japan

OTHERS

1990~96 Associate Editor Seitai Zairyo
(The Biomedical Materials Society, Japan)

1994~97 Section Editor: Bulletin of the Chemical Society, Japan
1997~ Associate Editor: Journal of the Society of Fiber Science and
 Technology
1998~ Associate Editor: Chemistry Letter (The Chemical Society, Japan)

Kazuyuki KURODA

Professor

Department of Applied Chemistry, Waseda University

Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan

Phone & FAX: +81-3-5286-3199,

e-mail: kuroda@mn.waseda.ac.jp

EDUCATION

1974	B.S., Applied Chemistry, Waseda University
1976	M.S., Applied Chemistry, Waseda University
1979	Ph.D., Applied Chemistry, Waseda University

PROFESSIONAL APPOINTMENTS

1979-1982	Research Associate, Waseda University
1982-1984	Assistant Professor, Waseda University
1984-1989	Associate Professor, Waseda University
1989-	Professor, Waseda University

EDITORIAL ACTIVITIES

1993-1994	J.Ceram.Soc.Jpn. (Editor in Chief)
1995-1998	Quarterly Chemical Reviews in Japan, (CSJ, Editorial Board)
1995-1997	Zeolite Society News (Japan Zeolite Association, Editor in Chief)
1995-	J. Porous Materials(Kluwer, Editorial Board)
1997-1999	Microporous Materials(Elsevier, Editorial Board)
1998-	Chemistry of Materials (ACS, Advisory Board)
1999-	Chemical Communications (RSC, International advisory board)
2000-	Microporous & Mesoporous Materials (Elsevier, Regional Editor Asia)

MEMBERS

The Chemical Society of Japan
The Ceramic Society of Japan
The Society of Polymer Science, Japan
The Clay Science Society of Japan
Clay Minerals Society(U.S.)
American Chemical Society, etc.

AWARDS

1994	The Award of Synthetic Chemistry of Catalysts
1996	The Award of the Clay Science Society of Japan

RESEARCH INTERESTS

Inorganic Materials Chemistry, Intercalation Chemistry, Silicate Chemistry, Inorganic Polymers, Sol-gel Chemistry, Porous Materials, Inorganic-Organic Nanocomposites

Richard M. LAINE

Professor

Depts. of Materials Science and Engineering, and Chemistry
and Macromolecular Sci. and Eng. Center

University of Michigan

Ann Arbor, MI 48109-2136, U.S.A.

(313) 764-6203, FAX 763-4788

email: talsdad@umich.edu

Academic Degrees and Educational Background:

- 1974-76 Postdoctoral Fellow--Professors P. C. Ford (Dept. of Chem.) and Prof. R. G. Rinker (Dept. Chem. and Nucl. Eng.) Univ. of Calif. at Santa Barbara, CA.
1973-74 Postdoctoral Fellow-- R. F. Heck, Dept. of Chemistry, University of Delaware.
1969-73 Ph.D. with Prof. Robert Bau, Univ. of Southern California, Los Angeles, CA.
1965-69 B.S. Cum Laude in Chemistry, California State Univ. at Northridge, CA.

Professional Appointments:

- 1990- Associate Professor, Dept. of Mat. Sci. and Eng., University of Michigan
1987-90 Research Professor, Dept. of Mat. Sci. and Eng. and, Director of Polymeric Materials Laboratory, Adv. Mat. Prgrm. Washington Technology Center (WTC)
1984-87 Associate Director of Inorganic and Organometallic Chemistry Programs--SRI Int.
1982-84 Senior Chemist--Organometallic Chemistry Group-SRI International.
1976-81 Chemist--Dept. of Organic and Inorganic Chemistry--SRI International.

Scientific and Professional Societies:

- American Chemical Society, Inorganic (Organometallic) and Polymers Divs. Polymer Div. Representative to Catal. Secretariat (1991-96)
Polymer Div. Representative to Mater. Secretariat (1996-)
Secretary General of Materials Secretariat (2000-2)
- The Materials Research Society
- The American Ceramics Society;
Vice Chairman (1994), Chairman, Michigan Section (1995)
- Associate Editor, Applied Organometallic Chemistry (1990-)
- Editorial Board, Materials Chemistry (1997-)

Honors (1990-):

- 1999--Invited Professor, Max Planck Institut for Metallforschung, Stuttgart, Germany

1998--Outstanding Research Award, Dept. of Mater. Science and Eng., Univ. of Michigan
1997--Invited Professor, Facultad de Ciencias, Universidad de Cadiz, Andalucia, Spain
1995--Visiting Professor, The Petroleum and Petrochemical College, Chulalongkorn University Bangkok, Thailand
1993--Visiting Professor, Petroleum and Petrochemical College, Chulalongkorn Univ.
1992--Professor Invite', Laboratoire de la Matière Condensée, Univ. Paris VI

Research Interests:

- Inorganic and hybrid polymer syntheses
Ceramics processing via precursor routes
Processing polymer and ceramic thin films and fibers

Krzysztof Matyjaszewski

Address

Business: Carnegie Mellon University
Department of Chemistry
4400 Fifth Ave, Pittsburgh, PA 15213
(412) 268-3209; fax (412) 268-6897

Home: 9 Queens Court
Pittsburgh, PA 15238
(412) 963-6591

email: km3b@andrew.cmu.edu www: <http://www.chem.cmu.edu/Matyjaszewski.html>

Personal Data

Born April 8, 1950, in Poland. Married with two children, US citizen

Education

Polytechnical University of Lodz, Poland, Habilitation, 1985
Polish Academy of Sciences, Ph.D., 1976 (Prof. S. Penczek, Thesis Advisor)
Technical University of Moscow, B.S./M.S., 1972

Experience

06.1998	present	J.C. Warner Professor of Natural Sciences, Carnegie Mellon University
07.1994	06.1998	Head, Chemistry Department, Carnegie Mellon University
07.1993	10.1985	Professor, Associate and Assistant Professor Carnegie Mellon University
04.1985	10.1985	Invited Professor, University of Paris, France
04.1984	04.1985	Research Associate, CNRS, France
03.1978	04.1984	Research Associate, Polish Academy of Sciences
03.1977	03.1978	Post-doctoral Fellow, University of Florida
09.1972	03.1977	Research Assistant, Polish Academy of Sciences

Awards

1999	Humboldt Award for Senior US Scientists
1998	Elf Chair of French Academy of Sciences
1995	Carl S. Marvel - Creative Polymer Chemistry Award (ACS)
1989	Award of Presidential Young Investigator (NSF)
1981	Award of Polish Academy of Sciences
1980	Award of Polish Chemical Society
1974	Award of the Scientific Secretary of Polish Academy of Sciences

-Visiting Professor at University of Paris (1985, 1990, 1997, 1998), University of Freiburg (1988), University of Bayreuth (1991), University of Strasbourg (1992), University of Bordeaux (1996),
-Reed Lecturer, Rensselaer Polytechnic Institute (1998), Milkovitch Lecturer, University of Akron (1998)
-Editor: "Progress in Polymer Science", Member of Senior Advisory Board: "Journal of Macromolecular Science";
Member of Editorial Boards of "Macromolecular Chemistry and Physics", "Macromolecular Rapid Communications", "Macromolecular Synthesis", "Journal of Polymer Science", "Journal of Inorganic and Organometallic Polymers", "Macromolecular Reports", "Journal of Macromolecular Science, Pure and Applied Chemistry", "International Journal of Polymeric Materials".
-Corresponding Member of IUPAC Commission on Polymer Nomenclature; Chairman of the Polymer Curriculum Development Award Committee, ACS; Member of Program Committee, Polymer Chemistry Division, ACS
-Coauthored/edited four books, twenty seven book chapters, over four hundred fifty scientific papers and twenty five patents. Current group consists of eight graduate students and five postdoctoral fellows.

Research Interests:

1. Synthesis of well defined macromolecules via living and controlled polymerizations. Radical, cationic, and anionic polymerization of alkenes and heterocyclics. Block, graft and gradient copolymers. Control of chain microstructure and topology. Functional polymers and telechelics.
2. Organometallic polymers. Polysilanes and polyphosphazenes. Preparation of well defined polymers and inorganic/organic hybrids with potential applications as nonlinear optical materials, photoconductors, photoresists. precursors to ceramics and biomedical materials.

Keiichi Moriya
Associate Professor
Department of Chemistry, Faculty of Engineering, Gifu University
Yanagido, Gifu 501-1193, Japan
Phone: +81-58-293-2569 Fax: +81-58-230-1893
e:mail: moriya@apchem.gifu-u.ac.jp

Personal

Date of birth: July 22, 1949
Family: single
Home: 4-7-7-401 Yabutaminami, Gifu, 500-8384 Japan
Phone: +81-58-277-5917

Education

1973 B.S., Chemistry, Faculty of Science, Osaka University
1976 M.S., Inorganic and Physical Chemistry, Osaka University
1982 Ph.D., Inorganic and Physical Chemistry, Osaka University

Personal Appointments

1984 August- 1984 November
Research Associate, Department of Chemistry, Faculty of Science,
Osaka University
1984 November- 1988 March
Research Associate, Department of Chemistry, Faculty of
Engineering, Gifu University
1988- Associate Professor, Department of Chemistry, Faculty of
Engineering, Gifu University

Members

The Chemical Society of Japan
The Society of Polymer Science, Japan
The Physical Society of Japan
American Chemical Society

Research Interest:

Physical Chemistry; Phase Transition and Molecular Motion in Solids and Liquids
Crystals; Inorganic and Organic Hybrids and Their Polymers

Dr. Masaki Narisawa

Department of Metallurgy and Materials Science
College of Engineering, Osaka Prefecture University
Sakai, Osaka 599-8531, Japan

Education:

BA degree in chemistry from Tohoku University, 1984.

Ph. D. degree in polymer chemistry from Tohoku University, 1989

Professional Experience:

Researcher

Super High Temp. Lab. , Government Industrial Research Institute,
Osaka (GIRIO), now Osaka National Industrial Research Institute
(ONRI), of MITI, 1989-1992

"Study of High Temperature Mechanical Properties of Carbon
Materials."

Research Associate

Department of Metallurgy and Materials Science, College of
Engineering, Osaka Prefecture University, 1992-

"Study of Precursor Chemistry for Silicon Carbide Materials."

Research Interests:

Materials Chemistry and Heat Resistant Ceramics

Professional Activities:

Member: The Ceramic Society of Japan; The Society of Polymer
Science, Japan; The Japan Institute of Metals; The Carbon Society of
Japan; The Materials Research Society of Japan

Secretary of a Kinki regional branch of "The Japan Institute of Metals."
(1993-1994).

A Vice-Chairman & a Committee of Research Group on Inorganic
Polymers in "The Society of Polymer Science, Japan." (2000-)

Papers and Reports:

29 papers, 10 proceedings or reports, 3 books (co-author of a chapter)

CURRICULUM VITAE

Name in Full: Yoshiyuki Sugahara

Date of Birth: September 15, 1960

Education:

- 1979-1983 Department of Applied Chemistry, School of Science and Engineering,
Waseda University (Bachelor degree of Engineering in March 1983)
- 1983-1985 Department of Applied Chemistry, School of Science and Engineering,
Waseda University (Master degree of Engineering in March 1985)
- 1985-1988 Department of Applied Chemistry, School of Science and Engineering,
Waseda University (Doctor degree of Engineering in March 1988)

Occupational Experience :

April 1987-March 1990

Research Associate at Department of Applied Chemistry,
School of Science and Engineering, Waseda University

September 1989-March 1990

Postdoctoral position at Department of Chemistry of
Massachusetts Institute of Technology (U.S.A.)
(Supervisor: Prof. Dietmar Seyferth)

April 1990-March 1992

Assistant Professor at Department of Applied Chemistry,
School of Science and Engineering, Waseda University

April 1992-March 2000

Associate Professor at Department of Applied Chemistry,
School of Science and Engineering, Waseda University

May 1998-October 1998

Visiting Scientist at Département de Chimie Organique Fine
Précurseurs organométalliques de matériaux
Université Montpellier II (France)
(Supervisor: Prof. Robert J. P. Corriu)

April 2000-Present

Professor at Department of Applied Chemistry,
School of Science and Engineering, Waseda University

Office Address

Department of Applied Chemistry, School of Science and Engineering, Waseda
University

3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169 8555, JAPAN

Tel/FAX: +81 3 5286-3204

E-mail ys6546@mn.waseda.ac.jp

BIOGRAPHICAL SKETCH

Richard A. Vaia, PhD
Air Force Research Laboratory
Materials and Manufacturing Directorate
AFRL/MLBP, Bldg 654
2941 P St.
Wright-Patterson AFB, OH 45433-7750
v: 937-255-9184
f: 937-255-9157
richard.vaia@afrl.af.mil

Rich Vaia is currently the Polymer Photonic Direction Leader and the team lead for Nanostructured Materials at the US Air Force's Materials Directorate at Wright-Patterson AFB, Dayton OH. He received a PhD from Cornell University in 1995. Since joining the research team at the Materials and Manufacturing Directorate, Dr. Vaia has directed in-house experimental and computational programs to explore the structural, electrical and nonlinear optical properties of polymeric materials and nanocomposites. He currently holds 2 patents and over 30 peer-reviewed journal articles.

BIOGRAPHICAL SKETCH

Ulrich B. Wiesner
Department of Materials Science and Engineering
Cornell University
329 Bard Hall
Ithaca, NY 14853
(607) 255-3487 ubw1@cornell.edu

Current Position: Associate Professor, Dept. of Mat. Sci. & Engr., Cornell, 3/99-present

Education:

Habilitation Phys. Chem., Dept. Chemistry & Pharmacy, University of Mainz, Germany, 1998
Ph.D. Phys. Chem., Max-Planck-Institute for Polymer Research, Mainz, Germany, 1991
Diploma Chemistry, Johannes Gutenberg University of Mainz, Germany, 1988

Positions:

Tenured Staff, Max-Planck-Institute for Polymer Research, Mainz, Germany, 5/98-2/99
Scientific assistant at the Max-Planck-Institute for Polymer Research, 5/93-4/98
Postdoctoral Associate, Laboratoire de Physicochimie Structurale et Macromoléculaire, associé au CNRS, ESPCI, Paris, France, 9/91-4/93

Awards and Honors:

Carl Duisberg Memorial Award of the German Chemical Society (GDCh), 1999
Travel Award of the German Chemical Society, Macromolecular Chemistry, 1996
Ph.D. Award of the Hoechst AG, 1991

Selected Publications

- 1.) K. Schuhmacher, C. du Fresne von Hohenesche, K. K. Unger, R. Ulrich, A. DuChesne, U. Wiesner, H. W. Spiess, *The synthesis of metal incorporated mesoporous molecular sieves of type MCM-48 with spherical morphology*, Adv. Mater. **11** (1999), 1194-1198
- 2.) R. Ulrich, A. Du Chesne, M. Templin, U. Wiesner, *Nano-objects with controlled shape, size and composition from block copolymer mesophases*, Adv. Mater. **2** (1999), 141-146.
- 3.) *Solid State NMR Studies of Organically Modified Ceramics*, M. Templin, U. Friedrich, U. Wiesner, H. W. Spiess, in: *Precursor-Derived Ceramics*, J. Bill, F. Wakai, F. Aldinger (Eds.), Wiley-VCH, Weinheim 1999, 205-213
- 4.) S. M. De Paul, J. W. Zwanziger, R. Ulrich, U. Wiesner, H. W. Spiess, *Structure, Mobility, and Interface Characterization of Self-Organized Organic-Inorganic Hybrid Materials by Solid-State NMR*, J. Am. Chem. Soc. **121** (1999) 5727-5736.
- 5.) M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schädler, U. Wiesner, *Organically Modified Aluminosilicate Mesostructures from Block Copolymer Phases*, Science **278** (1997), 1795-1798.

Kenneth J. Wynne

Professor of Chemical Engineering
Virginia Commonwealth University
Richmond, VA 23298
Ph: 804-828-9303
e-mail: kjwynne@vcu.edu

Ph. D., University of Massachusetts in 1965
Postdoctoral: UC Berkeley 1965-1967
Program Manager, Office of Naval Research, 1973- Feb 2000

80 Papers, 14 Patents, Co-edited 3 books

Research interests: polymer surface design and characterization, interactions of supercritical CO₂ with polymers; fluoropolymers; silicones; polymers with novel optical properties; electronically conducting polymers

Councilor, Polymer Division, ACS

Editorial Advisory Board Member: *Macromolecules*, *Journal of Applied Polymer Science*, the *Journal of Inorganic and Organometallic Polymers*, and *Polymers for Advanced Technologies*.